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THE CHEMICAL ACTION
OF LIGHT

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TORONTO

THE CHEMICAL ACTION OF LIGHT

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THE CHEMICAL ACTION OF LIGHT.

CHAPTER I.

Introduction. Radiant Energy.

EARLY HISTORY.

The influence of light on the formation of the green colour of plants and its bleaching action in the dark were probably noted by Aristotle (384—321 B. C.). Moreover Vitruvius reported on the bleaching of pigments by light (30 B. C.). The writings of the alchemists contain vague references to the action of light.

It appears that at the end of the 17th century, empirical study of the action of light began. Ray, the botanist, distinguished the action of light from that of air in plant growth. Bestucheff, the Prussian Chancellor, noticed that the colour of a solution of ferric chloride in alcohol was discharged in sunlight but recovered to some extent in the dark.

The brilliant investigator, Stephen Hales (1677—1721) was probably the first to suggest the influence of light in plant nutrition. A contemporary of Newton, Hales regarded light as a material substance, and asked, "may not light which makes its way into the outer surfaces of leaves and flowers contribute much to the refining of substances in the plant?"

J. H. Schulze, professor of medicine at Altdorf, was the first to study the light sensitiveness of silver salts, in 1727. Schulze was not seeking any photochemical action, but was trying to make a phosphorescent substance by treating chalk with nitric acid. By chance he used some nitric acid in which he had previously dissolved some silver. When he mixed this impure acid with the chalk, he happened to be standing near a window, and observed that wherever the direct sunlight fell upon the white mixture it was turned black immediately, while those parts which were sheltered from the sunlight remained unaltered. He repeated the experiment several times, but was dis-

appointed to find that a fresh sample of chalk and nitric acid did not show the action of light at all; he then happened to remember that the nitric acid which he used on the first occasion had been employed in dissolving silver. Therefore he dissolved a lot of silver in nitric acid and the darkening effects were greatly enhanced. Unfortunately, this observation of Schulze remained unnoticed. Priestley (*History and Present state of Discoveries relating to Vision, Light and Colours*, 1777) supported the corpuscular view of light in explaining the slow changes of colour of substances exposed to light.

Priestley noticed that plants confined in an atmosphere rich in fixed air (carbon dioxide) produced in the course of several days large quantities of dephlogisticated air (oxygen). Priestley explained the phenomenon as caused by the growth of the plants. In November, 1773, Pringle, then President of the Royal Society, in presenting Priestley with the gold medal of the Society, delivered an address in which he discussed the importance of Priestley's discoveries and the relation of plants to animal life on the planet in supplying oxygen.

About the same time, Scheele occupied himself with the same problem; but he arrived at results which were opposite to those of Priestley. While Priestley's plants improved the air due to the formation of oxygen, Scheele's plants produced carbon dioxide. We now know that the cause of this contradiction lay in the fact that neither Priestley nor Scheele realised clearly under what conditions the plant emitted oxygen or carbon dioxide. The Dutch physician Jean Ingenhousz published a very important memoir "Experiments upon Vegetables" in 1779, in which he established that the mere growth of a plant had nothing to do with the purification of the air. The plants were able to purify bad air in a few hours when subjected to sunlight. Ingenhousz discovered that plants in sunlight absorb air and exhale oxygen; that this action is the more active the brighter the sunlight, that in the shade the activity is less, while in the dark and at night, plants far from purifying the air, contaminate it as animals do. In his last important publication: "An Essay on the Food of plants and renovation of soils" (London 1796) he had quite freed himself from the phlogiston theory, and interpreted his results on the Lavoisier views. Ingenhousz saw clearly the cosmical function of green plants aided by sunlight, and the relation between animal and plant nutrition.

The experiments of Scheele (*Æris atque ignis examen Chemicum Upsala et Leps. 1777*) were far more important for the development of photochemistry. Scheele studied a large number of photochemical reactions, specially the blackening of silver chloride in light with the

liberation of chlorine. He was also the first to investigate the influence of the different parts of the spectrum, and observed that fused silver chloride (horn silver) became black first in the violet rays, which he attributed to the greater readiness with which those rays parted with phlogiston. Senebier's experiments (*Mémoires physicochimiques sur l'influence de la lumière*, Geneva 1782), carried on a few years after those of Scheele, are also of great importance. He observed that alcoholic tinctures of plant pigments, such as chlorophyll, were bleached by light, especially in presence of air. Berthollet, one of the founders of the law of mass action, observed the decomposition of chlorine water in sunlight (*Histoire de l'Académie Royale des Sciences de Paris* 290 (1785)); de Saussure (*Crell's Chem. Ann.* 356 (1796)) utilized this discovery in the construction of the first chemical actinometer. He also prepared actinometers from paper soaked in vegetable extracts for his meteorological observations on the Alps. In the essay on "Combustion" Mrs. Fulhame insisted that the presence of water was a necessary condition for the reduction of metals from their salts by light, which she considered as similar in behaviour to carbon, sulphur, and hydrogen; the salts reacted by the decomposition of water.

In 1800 W. Herschel made the important discovery of the infra-red region of the spectrum, and Ritter, in 1801, detected the action of ultra-violet rays on silver chloride, and observed that ultra-violet light is more active than visible violet rays. In 1802 Wedgwood and Davy attempted to take photographs on paper treated with silver salts, but could not fix them. Thomas Young showed by projection of Newton's rings on silver paper that ultra-violet rays behaved in the same way as the visible ones. J. B. Seebeck showed that silver chloride could, to a certain extent, reproduce the spectrum, specially after an initial exposure. Cruickshank in 1801 (*Nicholson's Journ.* 5, 202 (1801)) was probably the first to observe the formation of hydrochloric acid from a mixture of hydrogen and chlorine in light.

Gay Lussac and Thenard (1809—1810) investigated the influence of light on the combination of chlorine and hydrogen, and chlorine and ethylene, and they thought that the actions of light and heat were identical. Davy opposed this view and remarked that the violet and ultra-violet rays which have small heating effect are highly chemically active. In 1812 he investigated the photochemical formation of phosgene gas from carbon monoxide and chlorine. Davy also emphasized the view that the more refrangible rays exert a reducing action whilst the less refrangible ones have an oxidizing action. In his researches on

the nature of iodine and its compounds he observed the darkening of silver iodide in light.

The light-sensitiveness of a variety of other metallic salts continued to be investigated. Thus Planche (*Journ. de Pharm.* **449** (1815)) noticed that a mixture of ammonium oxalate and mercuric chloride is highly photosensitive, and Bradenburg (*Journ. f. Chem. and Phys.* **15**, 348 (1815)) studied the photosensitivity of manganese salts.

A great impetus to the study of photochemistry was given by Grotthus, who in 1818 endeavoured to combine the known facts of photochemistry in generalizations based on the electrochemical theories of Davy and Berzelius. The most important of his generalizations is known as the photochemical absorption law, which can be stated as follows: Only the rays absorbed are effective in producing photochemical change. Considering that light consisted of positive and negative electricities travelling side by side as $\pm e$, he assumed that a photochemical change was equivalent to a direct electrolysis, in which the components separated and combined respectively with the positive and negative electricities of light. The initial action of light upon a salt solution was thus to dissociate the salt into two parts, one of which was less soluble and the other more soluble than the original salt; for example a basic salt was precipitated from a solution of stannous chloride in water very much more rapidly in light. Similarly, calomel is precipitated from a mixture of ammonium oxalate and mercuric chloride, and ferrous oxalate from a solution of ferric oxalate. The more soluble product, according to Grotthus, is the acid component which is liberated. In oxygen or chlorine compounds, decomposed by light, Grotthus assumes that light de-oxidizes or dechlorinates the electropositive constituents, or prevents their oxidation. In either case, light is assumed to exert the inverse action on the inert electro-negative substance. A ray of light is, therefore, a line along which the elements of neutral electricity arrange themselves in polar fashion. There is no actual separation but the tendency to separation exists.

Henceforth increasing numbers of photochemical reactions were studied. Chevreul in 1837 published an important paper on the influence of air and moisture in the bleaching of vegetable colours in light. The researches of de Niepce and Daguerre carried on between 1814—1830, which led to the foundation of practical photography, are of great importance. Draper in 1839 emphasized the importance of the principle of Grotthus that absorption is the determining factor in the chemical effects of light. Biot (*Compt. rend.* **8**, 259 (315)) and Malaguti (*Ann. chim. et phys.* **72**, 5 (1839)) observed that many trans-

parent substances can markedly reduce the photochemical effect, and this was adduced as evidence of the retention of chemically active rays, which are really the ultra-violet radiations. E. Becquerel (*ibid.* (3), 9, 263 (1843)) observed that silver chloride behaves differently in different parts of the spectrum. Ritter, Herschel, Draper, and Becquerel emphasized the views of Davy that radiations of great refrangibility exert a reducing action as opposed to the oxidizing action of the longer wavelengths. In 1854 Bunsen and Roscoe started their classical researches on the photochemical combination of chlorine and hydrogen, which have played an important part in the scientific development of photochemistry. It is now known that by a suitable modification of the absorbing substance almost all radiations can exert chemical action. An important practical step in this direction was taken by H. W. Vogel in 1873, who observed that by mixing suitable colouring matters, silver salts could be made sensitive to green and yellow light, and thus a practical basis of colour photography was established.

INTRODUCTION.

Photochemical reactions take place when a reacting system receives from an external source radiation of a frequency which is not available in the system itself. The science of photochemistry has been concerned more specially with the reactions caused by the light of the visible and ultra-violet spectrum. The visible and ultra-violet radiations only represent a small fraction of the electromagnetic waves known to be given out by a vibrating system. Few experiments have been carried out regarding the influence of infra-red radiations on the one hand or X-rays, on the other, on chemical reactions.

In the following table the wavelengths of the various electromagnetic radiations now known are recorded:

TABLE.

Region	Wavelength
Cosmic ray	0.001 Å
Gamma ray from radium . . .	0.01 to 0.1 Å
X-ray	0.1 to 50 Å
Millikan-Osgood region	200 Å
Lyman region	600 Å
Schumann region	1300 Å
Ultra-violet	1850 to 3900 Å
Violet	3900 to 4240 Å
Blue	4240 to 4920 Å
Green	4920 to 5350 Å

TABLE (Continued).

Region	Wavelength
Yellow	5350 to 5860 Å
Orange	5860 to 6470 Å
Red	6470 to 7500 Å
Infra-red.	7500 to 3×10^6 Å
Rest-Strahlen	
Electric waves.	3×10^6 to 10^7 Å
Hertzian waves	10^7 to 10^{13} Å

In other words, the colour spectrum ranges from 0.00075 mm. for red to 0.00040 mm. for violet, and 0.00012 mm. for extreme ultra-violet, which is usually the lower limit for metallic arcs. The wavelength most suitable for sterilization is 0.00028 mm.

It will be evident from the above table that visible radiations consist of only a single octave. It should be mentioned here that the term light not only includes visible radiations but also infra-red and ultra-violet. The energy represented by electromagnetic waves has been termed radiant energy. Its effect varies with the wavelength and the nature of the substances undergoing a change. In most cases, the light absorbed by a substance is simply converted into heat, but it can also produce chemical transformation and the phenomenon of ionization. From the point of view of chemical action, the visible and ultra-violet rays are the more important. The infra-red radiations are only slightly active, whilst the influence of X-rays and of other radiations have not been sufficiently studied. The subject of photochemistry has received a powerful stimulus through the study of ultra-violet radiations and their application to industry.

MEASUREMENT OF RADIANT ENERGY.

We shall briefly indicate the general principles of the measurement of radiant energy in photochemical reactions. The term intensity of the radiant energy denotes the quantity of energy which passes in a unit of time through a unit of surface perpendicular to the direction of rays. Sometimes it is necessary to measure the absolute value of the intensity expressed as ergs or calories, but very often relative measurements are sufficient. Moreover, it is sometimes necessary to measure not the total intensity but that of certain rays. Thus in the question relating to ordinary illumination, the visible rays are specially important; and in photochemical operations, the active radiations, which vary with the nature of the reaction, are considered to be important.

The methods of measurement of radiant energy can be divided into three principal groups according to the nature of the radiation: (1) Photometry, which is based on the physical action of light. (2) Radiometry, in which the radiant energy is measured by the quantity of heat the radiation produces in a body which absorbs it. (3) Photochemical actinometry, in which the chemical action of light is utilized.

PHOTOMETRY.—Ordinary photometric methods are specially utilized for measuring the power of a light source. The intensity of a light source is compared with another taken as unity. Amongst the lamps which are used as standards the following may be mentioned: Carcel lamp which burns 42 grs. of rectified oil of colza per hour, and Hefner-Alteneck lamp, in which amyl acetate is burnt. Hefner-Alteneck unity is about $\frac{9}{10}$ of Carcel. Ordinary photometric measurements are not much utilized in photochemistry, because they do not supply sufficient information regarding photochemical reactions. These measurements are only applicable to visible light and are limited to the comparison of radiations of the same colour.

The relative intensity of radiations of different wavelengths cannot be directly measured photometrically but can be measured radiometrically. The photometric methods can, however, be adopted for comparison of two rays formed from a mixture in different proportions of radiations of different wavelengths. It is sufficient to decompose the two radiations into their spectra, and then successively compare the intensities of the spectral regions having the same colour. For these measurements, different types of spectro-photometers have been utilized. The most frequently used is that of König, which has been perfected by Martens and Grunbaum. For the investigation of the ultra-violet spectra, ordinary photographic plates are used, but occasionally screens which become fluorescent are also employed.

RADIOMETRY. — Radiometric methods are the only ones by which measurements of infra-red radiations and absolute measurements of radiant energy are possible. When a great sensitivity is necessary, the bolometer, or the thermoelectric pile, or the radiomicro-meter is used.

The bolometric method is based on the fact that the electric resistance of a wire increases with increase of temperature. Metallic wires or very thin leaves are utilized. Four similar pieces of wire or bands are placed in the branches of a Wheatstone bridge, and the resistances are adjusted in such a manner that there is no current through the galvanometer. When one of the wires is exposed to light the galvanometer is deflected proportionally to the intensity of the radiation. This

method is used for a relative measurement. For absolute measurements there are several methods. In the method of Ångström and Kurlbaum, one of the wires receives the radiant energy, whilst another wire identical with the first is heated by an electric current which does not disturb the galvanometer. The intensity of the current is regulated in such a manner that the galvanometer needle is at zero when thermal equilibrium is established. When this is realized, the two wires receive the same amount of heat per second in the form of electricity or light energy. Now we know that the quantity of heat produced per second in a wire traversed by a current is given by the relation:

$$q = 0.239 Ri^2.$$

The quantity of energy received by the other wire is thus known because it has the same value.

(1) THERMOPILE:—It is well known that a thermoelectric pile is composed of a certain number of couples of two metals (iron-constantan, for example).

When the junction between two metals is heated an electric current is generated. This phenomenon is of very great practical importance because it is employed in the construction of thermopiles. Generally thermopiles are made of about twenty junctions of bismuth and silver, or iron and tellurium or constantan. These junctions are blackened for the absorption of the infra-red radiations. Coblentz has improved the sensitivity of this apparatus. Very sensitive thermopiles and galvanometers are used with the infra-red spectrograph for the detection and absorption of infra-red rays. Generally, the Paschen, Broca, or Thomson galvanometer is used. In order to determine the quantum efficiency of a particular reaction, the Moll thermopile and galvanometer are being utilized for the measurement of absorption of incident radiations by the reacting system. For absolute measurements, the instrument should be standardized by means of a light source of known power. For this purpose the Hefner-Alteneck lamp is utilized. According to the measurements of Ångström, the total quantity of energy received from the lamp per second on a square centimeter of surface placed at right angles to the direction of the rays at a distance of one metre = 215×10^{-7} gram calories or 900 ergs. Recent measurements of Gerlach give the value 225.3×10^{-7} gram-calories. If A_1 represents the deviation of the galvanometer produced by the Hefner-Alteneck lamp placed one meter away from the thermopile, and A the deviation produced by the light under investigation, then the

absolute intensity of this light i.e. the amount of energy which it throws on to one square centimeter of the surface of the pile is given by the relation:

$$q = \frac{215 \times 10^{-7}}{A_1} \cdot A \text{ gram-calories.}$$

Recently Coblenz has prepared a thermocouple in a vacuum, and it has been claimed that the vacuum thermocouple is approximately three hundred times more sensitive than an ordinary thermocouple. The vacuum thermocouple has been utilized in measuring the light given out by stars.

(2) **RADIOMICROMETER.**—This instrument was first used by Boys and Paschen. It combines the advantage of both the thermopile and galvanometer, and therein lies its importance.

The original instrument consisted of a bismuth and silver thermocouple, connected to a copper wire, and suspended between the poles of a fixed magnet. When the thermocouple receives heat, it gives rise to an electric current, which passes through the copper wire and is deflected in the magnetic field. The whole suspension is very light and sensitive, hence it is influenced by external heat and vibration. Therefore, the zero error of the instrument is generally great.

These disadvantages of the Boys radiomicrometer have been practically overcome by Schaeffer, Paulus, and H. C. Jones (*J. Amer. Chem. Soc.* **37**, 776 (1915)). They have added a second thermocouple of exactly the same type as the first one, but acting in opposition to it. The external heat now affects both the thermocouples equally but in opposite directions, so that the zero error is eliminated.

To use this instrument for the measurements of absorption of the incident radiation, a lamp and scale are also necessary. The instrument is calibrated by means of either a Hefner lamp or black body radiation, for the amount of energy absorbed in producing 1 mm. deflection on the scale behind it.

CALIBRATION OF THE INSTRUMENT. — 1. *By Hefner lamp:*—A Hefner lamp is used under standard conditions. The energy according to Gerlach (*Physik. Z.* **14**, 577 (1913)) obtainable from it at a distance of one metre is 900 ergs per second per square centimeter.

2. *By black body radiation.* The black body radiation is obtained from a metallic cube coated with lamp black and containing water which can be heated underneath. A thermometer is immersed within the cube to indicate the temperature of the water inside. Use is made of the formula of Lummer and Pringsheim for a black body radiation,

$s = \sigma (\Theta^4 - T^4)$, with the condition that only one half of the energy radiated by the total surface of the cube facing the radiomicrometer is effective in producing deflection.

PHOTOCHEMICAL ACTINOMETRY.—Originally the word actinometry was used to designate the methods of measuring solar radiation. One of the oldest of these methods, which was invented by Draper and improved by Bunsen and Roscoe, was based on the observation of a chemical change produced by light. Hence the name actinometry has been used for photochemical photometry whatever the source of the radiation used.

By this method the ratio of the intensities of two radiations can be determined only when their spectral compositions are the same. Moreover, a photochemical change, to be used as an actinometer, should satisfy certain conditions. It is convenient to have a reaction which follows the Grotthus-Draper law, but theoretically there is nothing against the application of a reaction as an actinometer when the velocity is proportional to the square root of the incident radiation. The only essential things are exact knowledge of the ratio between the intensity and the velocity of the reaction, and that the same amount of light produces the same photochemical effect, which can be easily determined experimentally. It is desirable to avoid reactions which are highly sensitive to the influence of catalysts. Moreover, the absorption of light should remain constant during the time of measurement, so that the velocity remains constant for a definite light intensity. This last condition is realized when the absorption of light is complete. If the absorption is partial, the concentration of the reacting substances should remain practically constant. If this cannot be realized, a correction should be applied to the measurements. Constancy of light absorption is not, however, necessary for actinometers based on the use of photographic papers.

The first actinometer was used by Draper (*Phil. Mag.* (3), **23**, 401 (1843); **27**, 327 (1845)), who employed the combination of hydrogen with chlorine which is accelerated by blue and violet rays. The apparatus, to which Draper gave the name "thitonometer", had several defects, and his measurements were comparable only for a short interval of time. Bunsen and Roscoe (*Phil. Trans.* **146**, 355, 601 (1857); **148**, 879 (1859)) employed another experimental arrangement in which more precise measurements were possible. The gaseous mixture was placed in a spherical vessel filled with chlorine water. The hydrochloric acid formed by the action of light dissolved in the chlorine water. The progress of the reaction could be followed by observing the displacement

of a liquid index contained in a horizontal capillary tube fixed at the higher part of the reservoir. Under these conditions, the pressure of the gas remained constant during the time of the experiment. The photosynthesis of hydrochloric acid, however, is not a satisfactory reaction of actinometry, because it is very sensitive to the influence of different catalysts. The velocity of the reaction depends on the purity of the gaseous mixture, and for making really comparable measurements extreme care is necessary.

Amongst other reactions which have been employed in actinometry, we may mention the formation of mercurous chloride from ammonium oxalate and mercuric chloride (Eder mixture), which can be followed by determining the amount of calomel formed; the decomposition of oxalic acid in presence of uranyl salts; the reduction of ferric chloride by tartaric acid or lactic acid in methyl alcoholic solution (Benrath, Hess, and Obladen: *Z. Wiss. Phot.* **22**, 47 (1922)); the decomposition of laevulose under the action of ultra-violet rays (Berthelot and Gaudechon: *Compt. rend.* **156**, 707 (1913)); and the reaction between potassium oxalate and iodine (Dhar: *Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916)).

Different actinometers based on the blackening of photographic papers have been utilized by photographers, meteorologists, and naturalists. Bunsen and Roscoe (*Pogg. Ann.* **177**, 576 (1862)) have observed that the time necessary for producing a definite blackening of silver chloride varies inversely as the intensity. For obtaining the same blackening it is necessary that the product of the intensity and the time of exposure (I_t) should be constant. This relation, known under the name of the *Law of Bunsen and Roscoe*, forms the basis of the measurements by photographic actinometers. There are several types of these actinometers. A common defect of photographic actinometers is that their indications are uncertain and ill-defined. The velocity of blackening of a sensitive paper depends on the humidity of the air, and consequently the same amount of light produces different degrees of blackening according to the hygrometric condition of the air. On the other hand, a comparison of the intensities of light is only possible if the light has always the same spectral composition, and this condition is not generally satisfied by sunlight or diffused daylight. Certain radiations which act strongly on sensitive paper have but slight action on other systems or *vice versa*. Thus silver salts are very sensitive to violet light, but remain unaffected by red light, whilst both these radiations appear to be equally effective in causing carbon assimilation by plants in presence of chlorophyll. Thus the results of photographic

actinometers, if not cautiously interpreted, may lead to completely erroneous conclusions.

Recently, Webster, Hill, and Eidinow (*Lancet* **206**, 745, April 1924; compare L. Hill: *Proc. Roy. Soc. B.* **102**, 119 (1927)) have carefully carried out comparative tests of the chemical methods for the measurement of light intensity (actinometers) mainly from the view point of obtaining a standard in light therapy. The following actinometers were tested by them and proved unsuitable for their purpose:—

Eder's Photometer.—In this method a gelatin wedge of increasing greyness, with a scale printed beneath it, is used, and a light-sensitive paper of a standard make is placed in a frame beneath the wedge. On exposing the wedge to light, the extent to which the scale is printed off on the sensitive paper is a measure of the light intensity.

Bordier Actinometer.—Paper soaked in 20% aqueous solution of potassium ferrocyanide undergoes colour changes in light, and the amount of the change is determined by comparison with a set of standard colours, but this photochemical reaction seems to be very slow.

Keller's Modification of the Behring-Meyer test.—The mixture for exposure consists of: 25 c.c. 1% potassium iodide, 25 c.c. 5.3% sulphuric acid, 1 c.c. N/400 sodium thiosulphate, and a few drops of starch solution.

The time which elapses before the appearance of the blue colour is noted; unfortunately the test solutions are not very stable. This test gives results parallel with the erythema-producing power of different light sources.

Fürstenhaus' Actinometer depends on the change of electrical resistance occurring on illumination of selenium.

Paper treated with silver citrate darkens on exposure to light. This test, as well as the decompositions of pure dry hydrogen chloride, and aqueous solutions of hydrogen peroxide and cane sugar, were tried by Webster, Hill, and Eidinow.

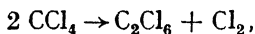
Sterilization of B. Coli.—100 c.c. of an emulsion of *B. Coli*, placed in a porcelain capsule 6 cms. in diameter, were exposed at a distance of 20 cms. from a quartz mercury lamp with and without a glass screen. The bactericidal action takes place about 1500 times as quickly without the interposition of the glass screen as with it.

Webster, Hill, and Eidinow remarked, "Seeking for a gauge based on the biological action we first began by trying the bleaching of various solutions of protein and methylene blue, and then turned to a solution of acetone-methylene blue as simpler and cleaner and having a suitable absorptive power. A solution of acetone in water is decomposed by ultra-violet light with formation of acetic and formic acids and other substances. We first used the increase in p_H of a watery solution of acetone exposed to a source of ultra-violet light as a measure of the light intensity, and in the laboratory this gives satisfactory results, although some care is needed. The decomposition of aqueous acetone in light is partly an oxidation process, and it was

thought likely that reduction processes were occurring at the same time, and that these might be measured by the reduction of methylene blue. This proved to be the case, the bleaching of the methylene blue being proportional to the time of exposure". The temperature coefficient of this reaction between 1.5° and 35° is about 1.17 for a 10° rise.

A small quartz tube is filled with the test solution consisting of 5.8 c.c. of 0.1% solution of Poulenc Frères' methylene blue and 30 c.c. acetone made up to 100 c.c. with water. The tube is exposed to the light source for a definite period at a known distance, and the change of colour is determined with a set of colorimetric standards. The acetone-methylene blue solution in a 3 mm. layer transmits 3342 Å, partly absorbs 3132 Å of the spectrum of the mercury vapour lamp, and wholly absorbs rays shorter than 3132 Å. According to Henri (*Compt. rend.* **156**, 230 (1913)), the maximum absorption of pure acetone lies at 2706 Å.

Another reaction, which has been recommended for medical work by Mackenzie and King (*Practical Ultra-violet Therapy*, Benn, 1926) is the photo-decomposition of pure carbon tetrachloride. It should be emphasized that the test suggested by Mackenzie and King fails entirely if ordinary carbon tetrachloride is used. The pure compound decomposes on exposure to light with the liberation of chlorine, but ordinary carbon tetrachloride, which contains carbon disulphide (compare Massol and Faucon, *Compt. rend.* **159**, 314 (1914)) will absorb chlorine. The main reaction occurs as follows:



and radiations of wavelengths shorter than 2650 Å are assumed to be effective.

It has been suggested by Gillam and Morton (*J. Ind. Chem. Soc.* **46**, 415, 417 (1927)) that the photochemical decomposition of potassium nitrate ($\text{KNO}_3 \rightarrow \text{KNO}_2 + \text{O}$) may be used in measuring the intensity of ultra-violet radiations. Moreover, the reaction seems to be suitable for determining the bactericidal effect of light, which is assumed to begin with radiations shorter than 3000 Å. According to Warburg (*Z. Elektrochem.* **25**, 334 (1919)) the photochemical decomposition of KNO_3 has the following quantum yields:

Wavelength	Quantum yield
2070 Å	0.25
2530 Å	0.17
2820 Å	0.024

The quantum yield becomes very small when the wavelength increases. The light absorption by nitrate solutions commences at 3300 Å, rises to a maximum near 3000 Å, falls to a minimum near 2650 Å, and rises very rapidly beyond this point to 1930 Å. A very thin layer of a strong solution of potassium nitrate is sufficient to absorb all light of wavelengths shorter than 3000 Å. The nitrite formed in the reaction is estimated colorimetrically according to the Griess-Ilosvay test.

The photochemical decomposition of oxalic acid sensitized by uranyl salts has also been utilized as a suitable actinometer. This reaction was first investigated by Mathews and Dewey (*J. Phys. Chem.* **17**, 216 (1913)), and the details necessary for working as an actinometer have been supplied by Anderson and Robinson (*J. Amer. Chem. Soc.* **47**, 718 (1925)), and Moss and Knapp (*J. Ind. Chem. Soc.* **44**, 453 (1925)). Recently Atkins and Poole (*Sci. Proc. Roy. Dublin Soc.* **19**, 321 (1929)) have used the same actinometer in measuring daylight illumination along the coast and at sea.

Forbes (*J. Phys. Chem.* **32**, 482 (1928)) states: "Chemical actinometers should employ only photochemical reactions which are reproducible, which involve only one phase, and whose photochemical efficiency is known for each of a number of wavelengths. Silver-halide paper actinometers are extremely crude devices. The Bunsen actinometer is not reproducible, and the Eder actinometer forms a precipitate. The uranyl oxalate photolysis, in spite of complications, has many advantages. It is unfortunate that none of the reactions so carefully investigated by Warburg are convenient for general use.

Photogalvanic cells involve too many obscure phenomena to promise well as actinometers . . . Selenium and Thalofide cells have sensitivity peaks at the longer wavelengths and other drawbacks for photochemical work."

Dorcas and Forbes (*J. Amer. Chem. Soc.* **49**, 3081 (1927)) have described a self-integrating chemical actinometer for ultra-violet radiations. They have shown that reddish-purple corex glass, backed with one centimetre layer of 0.00025 M picric acid solution, transmits, at each frequency, a light wattage proportional to the efficiency in producing erythema (sun burn) in human skin.

Recently Hymas (*Quart. J. Pharm.* **2**, 281 (1929)) has made a comparative study of the three chemical actinometers depending on the decompositions of carbon tetrachloride, aqueous solutions of oxalic acid containing uranium sulphate, and potassium iodide-starch solutions when exposed to ultra-violet radiations. The results, however, are not very concordant.

calculated. The measurements in the infra-red and ultra-violet are more difficult.

Absorption spectra are usually represented graphically. The best method of representation is to plot the wavelengths or frequencies as abscissae, and the coefficients of absorption or their logarithms as ordinates.

RELATION BETWEEN ABSORPTION AND CHEMICAL CONSTITUTION.

✓ The absorption spectrum of a substance depends essentially on its constitution. Other factors usually exert a feeble influence. The absorption is frequently independent of the solvent. Thus potassium permanganate has the same spectrum in aqueous, methyl alcoholic, acetone, and acetic acid solutions. Following the rule of Kundt, a displacement of the bands towards the side of longer wavelengths has often been observed when the refractive indices of the solvents increase. In the case of iodine, where the absorption spectrum changes completely with the solvent, it is believed that molecular compounds are formed with the solvents. A similar explanation seems to be valid for the marked change of absorption which follows variation of temperature in the case of the fulgides. In absence of chemical transformations, the influence of temperature on absorption seems to be feeble.

In the chemistry of the colouring matters, relations between the absorption spectra and chemical constitution have been sought for. The question had originally a practical interest, but later on the general question was tackled not only with dyes but with other substances as well. The researches carried on primarily with organic substances are far from completely solving the problem. These researches have led to a certain number of empirical rules, which permit the utilization of the absorption spectra in the determination of the chemical constitution of organic substances, or conversely the prediction of the spectrum of a compound from its known constitution.

Concerning inorganic compounds, no definite relation between absorption and constitution is yet known.

It should be stated that for organic substances, the presence of an absorption band or a group of bands is connected with the existence in the molecule of a particular atomic grouping to which the name *chromophore* has been given. Among the atomic groupings which cause a selective absorption, the following may be mentioned:

Carbonyl ($=\text{CO}$), Carboxyl ($-\text{COOH}$), ethylenic ($=\text{C}=\text{C}=\text{}$), nitro ($\text{>C}-\text{NO}_2$), nitroso ($\text{>C}-\text{NO}$), azoic ($-\text{N}=\text{N}-$), benzenic, quinonic etc.

The position of an absorption band produced by a chromophore is not invariable; it depends on the other groupings in the molecule. The groupings which cause a displacement towards the longer wavelength side are called *bathochromes*, whilst those which shift to the ultra-violet are known as *hypsochromes*.

When a molecule contains two chromophores, they influence each other. When the groups are near, the two bands which characterize them are displaced towards the red without marked change in the intensity of absorption. If the two groups are distant, the positions of the bands are not changed but there is an exaltation of the absorption. From a critical investigation of the absorption spectra of numerous substances in the ultra-violet and infra-red, V. Henri (*Structure des molécules*, Paris 1925) has given precision to the magnitude of these displacements and the variations of the absorption coefficients, and has been able to calculate with a good deal of exactitude the absorption spectra of a series of compounds containing the chromophores: carbonyl, carboxyl, and ethylenic linkings (e.g. oxalic, succinic, crotonic, and laevulic acids). Certainly it is not without interest to know the atomic groupings which cause the absorption of light leading to photochemical change, but this knowledge does not help us in understanding the mechanism by which light causes a chemical change. It is clear that a molecule which absorbs radiant energy is modified, but the change is not of a chemical nature in the ordinary sense, and cannot be represented by the usual structural formulae. The nature of this change was until lately unknown. The new conceptions on the electronic constitution of matter have thrown a certain amount of light on this question. Although they do not permit us yet to form a precise image of the change undergone by the molecule in the process of absorption, the new ideas allow us to conceive the nature of the change, and the manner in which the stability of the molecular edifice is decreased and chemical reactions are brought about.

ABSORPTION OF LIGHT BY MONATOMIC AND POLYATOMIC GASES OR VAPOURS.

The emission of light is always due to the reversion of an electron towards a lower orbit within an atom, and the absorption of light by the atom leads to the transportation of a peripheral electron to a higher

orbit. The absorption always takes place in entire quanta. The only radiations that can be absorbed are those of which the quantum is just sufficient for driving the electron from a certain level to another possible level. This appears surprising. If it is conceived, however, that the radiations of a frequency too feeble for causing the transportation of an electron are without action, it is clear why a quantum is inactive even when its energy value exceeds the necessary amount. The fact that the absorption spectrum of a vapour under low pressure consists of perfectly clear lines indicates that only certain quanta of definite values are actually absorbed.

According to the law of Kirchhoff relating to the constancy of the ratio between the emissive and absorptive power, one can imagine that all lines of the emission spectrum might appear as rays of absorption. In reality, it is not so, and it is easy to understand why. For example, suppose the valency electron in sodium vapour occupies the $1s$ level. Those radiations are absorbed which are capable of transporting this electron from this level to a higher level. The number of possible displacements is limited by the principle of selection. The only displacements which really take place are those by which the electron passes through one of the p orbits, and thus only those radiations are absorbed which belong to the series $1s - mp$. Wood and Fortrat, in their experiment with sodium vapour, have obtained an absorption spectrum consisting of 58 lines belonging to the above series. Similar observations have been made by Wood with vapours of potassium, rubidium, caesium, and lithium. The radiations which do not affect an atom in the normal state can be absorbed by an excited atom. Thus, if the external electron of sodium has been transported by light through the $2p$ orbit, it can absorb the quantum which makes it pass from the $2p$ to the $3d$ state. Although such cumulative phenomena of absorption seem to have been observed, their probability is very small, because an electron remains only for a very short time on an external orbit before it reverts towards the interior. Numerous experiments have been made with the object of determining the duration of this active period, which seems to differ with different atoms and different energy levels of the same atom. Wien (*Ann. der Physik* **60**, 597 (1919); **66**, 229 (1921)) obtained the value 2.3×10^{-8} sec., and Dempster (*Astrophys. Journ.* **57**, 114 (1923)) 5×10^{-8} , for the hydrogen atom. Gerlach and Schutz (*Phys. Zeitschr.* **26**, 33 (1925)) obtained values of the order $10^{-7} - 10^{-9}$ sec. for sodium atoms at the $2p$ level and for the mercury atom at the $2p_2$ level. Compare Dhar (*Z. anorg. Chem.* **141**, 1 (1924)); Dhar and Mukherji (*Z. Elektrochem.* **31**, 283 (1925)). In its return to its normal position an electron can emit light when the excita-

tion is produced by the collision of electrons. This kind of emission, which immediately follows absorption, causes the phenomenon of fluorescence; but very often the absorbed radiant energy is converted into heat, i.e. kinetic energy of the atoms. The mechanism of this transformation is imperfectly known. However, there is no doubt that the transformation is caused directly by atomic collisions. An atom which has absorbed light energy can in its encounter with another atom use all or part of the quantum absorbed in increasing its velocity. The absorption spectra of vapours containing molecules with several atoms are more complicated. It has already been stated that polyatomic vapours under low pressures give band spectra consisting of lines near each other. Deslandres was the first to represent successfully the distribution of such rays by an empirical formula. A theoretical interpretation of these formulae based on the quantum theory was first attempted by Schwarzschild, who used as evidence the fact of rotational movement of molecules. The theory has been developed by Heurlinger and Lenz, and by V. Henri, who has also carried out numerous experiments. The molecules of a given substance can exist under different conditions, each characterized by a definite value of its energy content. This energy depends on the movement and the positions of the electrons and the atoms, as well as on the rotational movement of the molecule. A change of state consists occasionally of a variation of one of these movements. The energy of rotation can increase without appreciable modification of the internal state. But generally two or three of these movements are simultaneously affected by the absorption of a single quantum of light. Let us consider the case where the rotational movement of the molecules and the oscillatory movement of the atoms have come into operation. In a diatomic molecule, the 2 atoms can have an oscillatory movement relative to each other, according to the manner in which their centres are connected. If these vibrations are harmonic, their energy is equal to a number of entire quanta, and we have the relation $W_a = nh\nu_a$ where n is a whole number and ν_a the frequency of these vibrations. If the movement is not harmonic, and this is so when the molecule contains more than 2 atoms, the expression becomes more complex. On the other hand, the energy of rotation of a molecule can, according to the quantum theory, have the values given by the relation:

$$W_m = \frac{m^2 h^2}{8 \pi^2 I},$$

where I represents the moment of inertia of a molecule, and m the quantum number of the rotational movement. When the molecule

passes from a state characterized by the quantum numbers m, n to the state m', n' the increase in its energy is given by the relation

$$\Delta w = (n' - n) h \nu_a + \frac{h^2}{8\pi^2 I} (m'^2 - m^2). \quad (1)$$

According to the relation of Bohr ($\Delta w = h\nu$), the frequency of these radiations, the absorption of which causes the change of state, is given by the relation

$$\nu = (n' - n) \nu_a + \frac{h}{8\pi^2 I} (m'^2 - m^2) = (n' - n) \nu_a + B(m'^2 - m^2), \quad (2)$$

where

$$B = \frac{h}{(8\pi^2 I)}.$$

According to the principle of selection, the quantum number m can vary only by unity. On the other hand, the first term of the second member being much larger than the second, the case $n' - n = -1$ is excluded, because ν would thus become negative, and this would correspond to emission of light, but we are considering only the case of absorption of light. The only possible cases are

$$n' = n + 1 \quad \text{and} \quad m' = m \pm 1. \quad (3)$$

The expression (2) is thus simplified and becomes

$$\nu = \nu_a + B(\pm 2m + 1). \quad (4)$$

Finally, if only the energy of rotation varies, the formula becomes

$$\nu = B(2m + 1). \quad (5)$$

From recent work on wave mechanics, this equation reduces to $\nu = 2Bm$; a modification which takes place owing to the introduction of half quantum numbers. A negative value of $2m$ corresponds to emission of light.

The spectra of rotation, the frequencies of which are given by the above relation, are always situated very far in the infra-red, and are in the neighbourhood of 1,000,000 Å. The spectra of oscillation and of rotation represented by expression (4) consist of radiations of much higher frequency. They are still in the infra-red, but their wavelengths are of the order of 10,000 Å.

Thanks to the researches of Rubens, Miss E. von Bahr, Slater, Imes, and Eucken, these spectra are very exactly known for water vapour, HCl, HBr, HI. According to formula (5) the differences between the frequencies of the consecutive rays are constant. We get the following relation:

$$\nu_{m+1} - \nu_m = 2B = \frac{h}{4\pi^2 I}.$$

It will be seen that this relation permits the determination of the moments of inertia of the molecules. The difference ($\nu_{m+1} - \nu_m$) is the same in the spectrum of oscillation as in the spectrum of rotation. This has been verified by Eucken. One can conclude that the vibratory movements of atoms are not appreciably modified by their moments of inertia.

When the change produced in the molecule reaches the movement and the position of the electrons, the variations of the energy become much more marked, and the absorption bands appear in the visible or the ultra-violet. Moreover, the lines become very large and the relation of their distribution becomes more complicated. When a molecule of nitrogen, for example, absorbs a quantum which acts on the electrons, their dimensions increase and consequently also their moment of inertia. The last term of the formula (2) should be replaced by the expression:

$$-\frac{h \cdot (m \pm 1)^2}{8 \pi^2 I'} - \frac{h m^2}{8 \pi^2 I} = \frac{h m^2}{8 \pi^2} \left(\frac{1}{I'} - \frac{1}{I} \right) \pm \frac{h m}{4 \pi^2 I'} + \frac{h}{8 \pi^2 I'}.$$

Moreover, if the term ν , corresponding to the increase of energy of the electrons is introduced, the following relation is obtained:

$$\nu = \nu_e + \nu_a + \frac{h m^2}{8 \pi^2} \left(\frac{1}{I'} - \frac{1}{I} \right) \pm \frac{h m}{4 \pi^2 I'} + \frac{h}{8 \pi^2 I'},$$

and this can be expressed in the form $\nu = A \pm 2 B m + C m^2$. This parabolic equation accounts perfectly for the distribution of the lines in the absorption band of a diatomic molecule and their shift towards the longer wavelength side. In the absorption spectrum of nitrogen, there are 18 definite bands between 4606 and 3584 Å. For each of them, the term ν_e is constant.

The distribution of the lines in a band is not always represented by the above formula. The moment of inertia is not always changeable, and the term ν_e is not always constant. In the case of polyatomic molecules like those of benzene, naphthalene, etc., oscillations can take place in more than one way, and thus ν can have more than one value. Thus V. Henri has been able to identify in benzene vapour under low pressures, four series of lines represented by an equation of the form:

$$\nu = \nu_e + n a - n' b + n' b^2 + \frac{h}{8 \pi^2 I} (m'^2 - m^2).$$

The terms $n a$, $n' b$ and $n' b^2$ correspond to nonharmonic motion of the atoms. The moment of inertia is constant, whilst ν_e takes different

values in different series. These values of ν_e , however, remain very near each other (between 37,426c and 37,707c), and their variations are caused by the slight differences in the energy of the electron.

In future, the studies of band spectra are likely to throw light on the mechanism of the action of radiation in photochemical changes. We have stated that those radiations which only modify the rotatory movement of the molecules, or the vibrations of the atoms, belong generally to the infra-red. Now the infra-red radiations are ordinarily without much chemical action. The visible or ultra-violet rays only are capable of displacing the electrons, and are, also, as a rule, chemically active. Hence one can conclude that photochemical changes are ordinarily caused by the action of light on the electrons.

INFLUENCE OF AN INTERNAL FILTER.

When a substance, contained in a mixture which is sensitive to the action of light, absorbs thermally the active rays, it is called an internal filter or screen. The presence of such a substance naturally leads to the diminution of the amount of energy received by the photosensitive substance, and thus the velocity of the reaction is slowed down. This effect can be produced by the addition of a foreign substance to the mixture of which the concentration remains constant, or by a substance which is insensitive and disappears in the course of the reaction, or by a product of the reaction. In the oxidation of quinine by chromic acid (which is the acceptor), the part of the internal filter is played by chromic acid itself. In the reaction between potassium oxalate and iodine, KI_3 molecules, and in the oxidation of alcohol by chromic acid, sulphate of chromium, which is a product of the change, act as internal filters. Similarly the products formed by the oxidation of leucobases are assumed to act as internal filters.

We have already seen how the quantity of light absorbed, and its distribution amongst the two reacting substances, can be calculated in the case of a system containing two light absorbing substances. Starting from formulae (11), (12) (p. 17), one can easily find out that the quantity A , of the light absorbed by one of the two substances is given by the relation:

$$A_1 = \frac{i_1 c_1}{i_1 c_1 + i_2 c_2} \cdot S(I_0 - I_t) = S I_0 \cdot \frac{i_1 c_1}{i_1 c_1 + i_2 c_2} (1 - e^{-(i_1 c_1 + i_2 c_2) l}),$$

in which c_1 , c_2 , i_1 and i_2 represent the concentrations and the coefficients of absorption. If A_1 is connected with the photosensitive

substance, and if the photochemical effect is proportional to A_1 , the following velocity expression is obtained:

$$-\frac{dc}{dt} = K \cdot \frac{I_0 - I_l}{l} \cdot \frac{i_1 c_1}{i_1 c_1 + i_2 c_2} = \frac{K \cdot I_0}{l} \cdot \frac{i_1 c_1}{i_1 c_1 + i_2 c_2} (1 - e^{-(i_1 c_1 + i_2 c_2)l}) \quad (1)$$

This equation is simplified when the absorption is complete, and becomes $-\frac{dc}{dt} = \frac{K I_0}{l} \cdot \frac{i_1 c_1}{i_1 c_1 + i_2 c_2}$. If the absorption is feeble, the factor within the brackets in (1) becomes equal to $(i_1 c_1 + i_2 c_2)l$ and the following relation is obtained: $-\frac{dc}{dt} = K I_0 i_1 c_1$, which is the same formula as if there was no internal filter.

Luther and Forbes (*J. Amer. Chem. Soc.* **31**, 770 (1909)) verified relation (1) in their researches on the oxidation of quinine by chromic acid; a reaction which already had been studied by Goldberg, (*Dissertation*, Leipzig 1906) who came to the conclusion that chromic acid is the photosensitive substance and quinine is the acceptor. On the other hand, Luther and Forbes asserted that quinine is the photosensitive substance and chromic acid the acceptor, because the rays which are absorbed by quinine are photochemically active. The radiations of wavelength 4330 Å, which are strongly absorbed by chromic acid ($i_2 = 56$) but very weakly absorbed by quinine ($i_1 = 0.004$), are supposed to be inactive. Experiments were carried out with radiations of wavelengths 4660 Å and 3620 Å. The absorption coefficients of chromic acid and of quinine have been measured for each of these radiations. On applying the foregoing formula, Luther and Forbes were able to state that the photochemical effect is proportional to the absorption produced by quinine. A complication arises from the fact that there is a thermal velocity for this reaction, which is proportional to the product of the concentrations of the two substances. In calculating the photochemical velocity, the thermal velocity was deducted from the total velocity. It is interesting to note here that Luther and Forbes observed that for the same amount of light absorbed, the photochemical effect in radiations of wavelength 4060 Å was four times greater than that obtained with radiation 3620 Å. These results are doubtful, in view of the recent measurements of the velocities of this reaction in different radiations, undertaken by Dhar and collaborators.

It should be mentioned that chromic acid has often played the part of a photosensitive substance, as will be evident from the numerous photochemical reactions studied by Dhar and collaborators, with chromic acid and different reducing agents, in radiations of wavelengths

8500, 7304, 5650, 4725 Å. Moreover, Plotnikoff (*Lehrbuch der Photochemie*, p. 583) has made the interesting observation that light filtered through a solution of quinine sulphate can be active in the reaction between ammonium chromate and quinine sulphate. These facts show that the view of Luther and Forbes that only the light absorbed by quinine is active, is untenable.

The enfeeblement of the light intensity in a reacting medium can also be caused by the formation of a solid product, which may remain in suspension. The matter in the suspended condition not only absorbs light, but also scatters light, and the growth of the particles with time leads to a difference in the amount of absorbed and scattered light. Hence the production of a precipitate in the course of the reaction leads to considerable complication, and the formulae deduced previously are not applicable to this case.

GROTTIUS-DRAPER LAW.

In photochemical changes, light supplies the energy necessary for the activation of molecules. It is clear therefore that radiations which are not absorbed cannot cause a chemical reaction. This law was formulated as early as 1818 by C. J. D. Grotthius. It passed unnoticed and was reannounced by Draper in 1839. It has been confirmed by several workers, but is purely qualitative. This law does not express the mathematical function which connects the quantity of matter transformed with the amount of light absorbed.

In the 18th century, Senebier (1788) expressed the opinion that if the product of the light intensity and the duration of illumination is constant, the photochemical effect remains the same. The first experimental verification of the relation between the amount of chemical change and the quantity of energy absorbed was made by Draper (*Phil. Mag.* (3) **23**, 401 (1843); **27**, 327 (1845)) who studied the reaction between chlorine and hydrogen. These first measurements of Draper were not accurate, but they were repeated by Bunsen and Roscoe (1855—1857) with great care, who found that the quantity of HCl formed is proportional to the light intensity and the time, and can be expressed by the relation $Q = KIt$. In these experiments, the pressure and the composition of the gaseous mixture were constant. Wittwer in 1853 indicated that the velocity of the photochemical decomposition of chlorine water is proportional to the concentration of chlorine. The water being in excess, the same relation is expected from the law of mass action. We shall see later that this reaction is

really more complicated. Nernst (*Theoretical Chemistry*, 4th edition, p. 732) generalized the conception of Wittwer, and stated that the velocity of a reversible photochemical reaction represented by the general equation $n_1A_1 + n_2A_2 \rightleftharpoons n_3A_3 + n_4A_4$ can be expressed by the relation:

$$V = v - v' = K c_1^{n_1} \cdot c_2^{n_2} - K' c_3^{n_3} \cdot c_4^{n_4},$$

as in the dark. According to Nernst, light acts as a catalyst in some manner, and simply increases the coefficients K and K' ; and the influence of light would be proportional not to the quantity of light absorbed but to the light intensity. It appears, however, that the experiments of Wittwer alone, the validity of which is now questioned, are not sufficient for the enunciation of a theory of photochemical reaction. We have already stated that when light absorption is feeble, the velocity of a photochemical reaction is proportional to the concentration of the absorbing substance. This condition seems to have existed in the experiments of Wittwer. The two views (the velocity is proportional to the concentration of chlorine, or the quantity of light absorbed) are identical in this case. When the absorption is complete, the two hypotheses lead to different results. In 1903, Wildermann (*Z. phys. Chem.* **42**, 257 (1903)) attempted to discover which of the two views is correct. He carried out experiments on the formation of phosgene gas ($\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$), in a mixture containing variable proportions of CO and Cl_2 . The velocity was found by Wildermann to be proportional to the product of the concentrations of the two gases: —

$$\frac{d[\text{COCl}_2]}{dt} = K [\text{Cl}_2] [\text{CO}].$$

Wildermann concluded from his experiments that the law of mass action is applicable to photochemical reactions in agreement with the views of Wittwer and Nernst. We shall see later that the conclusions of Wildermann are erroneous. The hypothesis that the velocity of the formation of phosgene is proportional, on the one hand, to the quantity of light absorbed by chlorine, and on the other, to the concentration of carbon monoxide, has not been considered by Wildermann. Shortly after these researches, the view that the quantity of matter transformed increases proportionately to the amount of light absorbed was revived by the experiments of Luther and Weigert (*Z. physik. Chem.* **51**, 297; **53**, 385 (1905)) on the transformation of anthracene into dianthracene. As a matter of fact the view that the amount of chemical change is proportional to the light absorbed is not exactly applicable to the

above reaction, as the kinetics are complicated. Lasareff (*Ann. Physik.* **24**, 661 (1907)) was the first to emphasize a proportionality between the photochemical effect and the amount of light absorbed. The reactions studied by him were the decolorization of dyestuffs impregnated in collodion. This proportionality has also been found by Luther and Forbes (*J. Amer. Chem. Soc.* **31**, 770 (1909)) in the oxidation of quinine by chromic acid, and by Berthelot and Gaudechon (*Compt. rend.* **156**, 707, (1913)) in the decomposition of laevulose. The same relation has been observed in several other photochemical reactions.

The law which expresses the proportionality between the photochemical effect and the quantity of light absorbed is often called the law of Grotthus, although this author formulated only a qualitative relation. This law has also been called the law of Draper. In reality, this savant stated only a proportionality between the photochemical effect and the *incident light* ($I \times t$).

On the other hand, Lasareff, in his first experiments, did not measure the effect produced by different quantities of light of the same wavelength. He only compared the action of rays of different colours; and the proportionality, independent of the frequency, which he observed, is not to be found ordinarily. The law of proportionality with which we are now concerned has a different significance, because here the relation is concerned with radiations of the same wavelength. Hence it is apparent that there has been some confusion regarding the exact nature of the relation which is now known as the Grotthus-Draper law, although neither of these authors attempted to establish a quantitative relation between the absorbed light and the amount of chemical change.

In certain reactions, the photochemical effect is simply proportional to the quantity of light absorbed, and depends only on the concentration so far as the light absorption is influenced by change of concentration. In other cases, the phenomenon is less simple. The absorbed light is not the only factor to consider in such cases. The concentration of one or both the reacting substances has an influence independent of the change of light absorption already discussed. Finally, the law of Grotthus-Draper as we shall show later on, is not generally true.

THE LIMIT OF THE VALIDITY OF THE LAW OF GROTTTHUS-DRAPER.

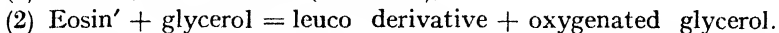
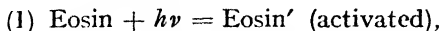
It is certain that this law is not always true, but can be looked upon as a rule rather than a law. In many reactions it has been ob-

served that the photochemical effect is not directly proportional to the light absorbed, and in some cases the proportionality factor between the amount of change and the energy absorbed depends on the concentration of the reacting substances. It will be emphasized in the subsequent pages that the velocities of several photochemical reactions are proportional to the square root of the intensity of the incident radiation, as well as to the energy absorbed. It is clear, therefore, that the law of Grotthus-Draper fails more frequently than one has hitherto imagined. Very often authors have taken it for granted that the law is valid for the reactions investigated by them, without making the necessary experimental tests. An experimental test is all the more necessary in such reactions as present some peculiarities, e.g. the reaction between sodium sulphite and oxygen in light appears to be proportional to the square root of the concentration of sodium sulphite. Similarly, several reactions with iodine as a reacting substance are proportional to the square root of the concentration of iodine. It is desirable that experiments should be made to find out whether the Grotthus-Draper law is valid for these reactions.

Some authors assume that the law of Grotthus-Draper is always applicable to the primary photochemical process, but attribute the observed deviations to secondary reactions. This view is undoubtedly correct for the process of actual activation, but this cannot be maintained if the primary photochemical process is believed to be the chemical transformation on illumination.

We have seen that the loss of the energy of a molecule can be hastened by shocks, or by the presence of foreign molecules such as the molecules of the solvent. The mean duration of the active state is thus reduced, and hence the quantum yield may also decrease. Moreover, there is also the possibility that active molecules may lose energy by coming in contact with inactive molecules of the same substance. It will be stated later on that Warburg attributes the decrease of the quantum yield in the ozonization of oxygen, when the pressure of oxygen is very high, to the loss of energy from the active molecules by collisions with the neighbouring inactive molecules. This aspect of the question has been emphasized by Perrin and Miss Choucroun (*Compt. rend.* **178**, 140 (1924)), and by Levailant (*ibid.* **177**, 398 (1923)). They have carried on researches with solutions of organic fluorescent substances. An aqueous solution of uranine is decolorized in light in presence of air. In glycerine solutions there is decolorization in light even in absence of air. Perrin and his collaborators have obtained similar relations with fluorescein, eosin, and methylene blue. Chakravarty and Dhar (*Z. anorg.*

Chem. **142**, 299 (1925)) have shown that most of the fluorescent and non-fluorescent dye-stuffs can be oxidized in light in presence of air, and most of these dyes are also reduced to colourless products when exposed to light with reducing agents like glycerol, glycol, sugars etc. Most of these reactions are apparently bimolecular, and the following processes are assumed to take place in the photochemical reduction of eosin by glycerol:



The experiments of Perrin and Miss Choucroun have shown that for the same quantity of light absorbed, the photochemical effect decreases with the increase in concentration.

If the photochemical effect were proportional to the quantity of absorbed light, the decolorization would proceed with the same velocity in all reaction vessels with the same amount of incident light. In reality this is not the case. With eosin containing equal proportions of water and glycerol the following results have been obtained:

Velocity of decolorization	325	30	9
Concentration of the dye	0.0004	0.002	0.02

With methylene blue in glycerol the following results were obtained:

Velocity of decolorization	600	300	90	5
Concentration of the dye	0.00002	0.0001	0.001	0.005

Consequently the velocity of decolorization under the experimental conditions of Perrin and Miss Choucroun should have been constant according to the law of Grotthus-Draper, but actually the velocity decreases very rapidly as the concentration is increased.

It is interesting to note that Perrin has obtained a similar relation in the decrease of fluorescence with increase of concentration of the dye. It is assumed that a quantum absorbed by a molecule makes it fluorescent or chemically reactive. The decrease of fluorescence with increase of concentration is attributed to the loss of the energy of activation by collision with neighbouring inactive molecules, and consequently, by the presence of a large number of inactive molecules, the life period of the active molecules becomes less, and the absorbed energy is lost as heat.

Perrin was thus led to believe that the decrease of photosensitivity with the increase of the concentration is a general phenomenon, just as in the case of fluorescence, and that the law of Grotthus-Draper is valid only for very dilute solutions. However, this conception does not

appear to be supported by the known facts concerning the kinetics of photochemical reactions. Only under exceptional circumstances does the duration of the life period of active molecules change with the concentration of the reacting substance; and the law of Grotthus-Draper is often applicable to solutions of fairly high concentrations, and to mixtures of gases where the pressure is not low. Although fluorescence and photochemical sensitivity are not exactly alike, there are certain common properties of molecules which become fluorescent or photochemically active. They are assumed to be in the Bohr state of activation, and those agents which accelerate the reversal of the fluorescent molecules to the ordinary state should also, according to Perrin, suppress the chemical reactivity. However, this is not generally true. A change in the concentration or composition of a solution does not affect the fluorescence and photochemical activity equally. The diminution of fluorescence by a foreign substance is occasionally attributed to the chemical activity of the foreign substance. The excited molecules can revert to the normal state by giving off the absorbed radiation, or can react chemically on giving out heat. The occurrence of the second phenomenon naturally diminishes the chance of the first, and hence the intensity of fluorescence is likely to be diminished by the occurrence of the chemical change. Thus Trümpler (*Z. physik. Chem.* **90**, 385 (1915)) observed that oxalic acid, which decomposes in light more rapidly than formic acid, in presence of uranyl salts, also extinguishes the fluorescence of uranyl salts more markedly than formic acid. Similarly, the fluorescence of an anthracene solution decreases as the concentration increases, and the velocity of dianthracene formation becomes more rapid. On the other hand, there are other phenomena, the explanation of which is not clear. Thus a solution of quinine sulphate becomes more fluorescent on acidification, and Luther and Forbes (*J. Amer. Chem. Soc.* **31**, 770 (1909)) observed that the photochemical oxidation of quinine by chromic acid is accelerated by acids, whilst Weigert (*Nernst Festschrift* 464 (1912)) showed that the oxidation of quinine by oxygen is retarded by H ions, and practically stops when the acid concentration becomes 0.1 normal. Moreover, even in the experiments of Perrin there is no exact parallelism between the variation of chemical activity and fluorescence. When the concentrations increase the velocity of decolorization decreases more rapidly than the fluorescence. Two solutions of methylene blue containing $\frac{1}{1000}$ and $\frac{1}{100}$ mol. give out the same fluorescent light, but the velocity of decolorization is double in the second case than in the first. The vapours of bromine and iodine cease to be fluorescent

when the pressure is feeble, but the photochemical sensitivity continues up to extremely low pressures. Consequently, it seems clear that photosensitiveness and fluorescence do not vary in the same proportion.

There is evidence in favour of the view that in many cases, the molecules of halogens are dissociated into atoms on illumination, and that the atoms are the active substances for photochemical reactions. Stern and Volmer (*Z. wiss. Phot.* **21**, 134 (1922)) have stated that a molecule of iodine can absorb a quantum of energy superior to that necessary for atomization without dissociation into atoms. They have concluded that the dissociation of a molecule in the Bohr state of activation can only take place when the active molecule enters into a collision with another molecule of the same or another substance. On the other hand, it is assumed that such collisions of active molecules with inactive ones lead to decrease of fluorescence but not of chemical activity. It is apparent from our experience in photochemistry that all photochemical substances are not dissociated by light, but it is quite possible that dissociation of a molecule into atoms is not the only phenomenon produced by light absorption, by which the activity induced by light is retained in some manner or other. Nevertheless, it can be assumed that all molecules, which have absorbed a quantum, react chemically. Hence the photochemical effect should, in certain cases, be independent of the duration of the active state. Moreover, the decrease of fluorescence with the increase of concentration is generally observed only with relatively concentrated solutions. Aqueous solutions of certain uranium salts, quinine sulphate, or of phenanthrene in benzene, are examples of the above phenomenon. Now the duration of the active state with or without fluorescence, decreases only with relatively concentrated solutions; the photochemical effect remains proportional to the quantity of the light absorbed even with fairly strong solutions of the photosensitive substance.

The above considerations show that the law of Grotthus-Draper is applicable to the primary photochemical process with the restriction already stated. Nevertheless it is quite possible that the phenomenon observed by Perrin will be evident in other photochemical reactions. Let us remember that Weigert showed that the velocity of decolorization of dyestuffs in collodion increases with the concentration more slowly than the amount of light absorbed; but this is concerned with solid systems, where the fluorescence does not decrease with increase of concentration as in the case of ordinary solutions.

THERMAL AND PHOTOCHEMICAL ABSORPTION.

Although a photochemical reaction can only take place by the absorption of light, light absorption is not always followed by a chemical transformation. Hence attempts have been made to distinguish between *thermal absorption*, in which the radiant energy is simply transformed into heat, and *photochemical absorption*, in which the absorbed radiation leads to a chemical change. It should be remarked, however, that light is converted into chemical energy only in those reactions which require energy. In numerous cases light only accelerates a chemical change which can take place in the dark.

As a rule the photochemical activity of light increases with its frequency; usually infra-red radiations have little photochemical activity. We shall discuss the question of the activity of infra-red radiation fully later on.

Chemical reactions sensitive to blue and violet rays are more frequent than those sensitive to red rays. Moreover, there are some reactions which are sensitive mainly to ultra-violet rays. The increase in the activity of light with its frequency has been explained on the view that a quantum of light having a high frequency contains more energy than a quantum of light of low frequency.

The photochemical sensitiveness of a system with regard to a definite frequency of radiation has been defined as the ratio of the amount of matter transformed to the quantity of incident light. V. Henri and Wurmser designate this ratio as *photochemical susceptibility*. This sensitiveness appears to be a complex function of the frequency of light. Although only the absorbed radiations are photochemically active, the variations of the susceptibility with the wavelength essentially depend on the absorption spectrum of the system. However, not all the absorption bands correspond to maxima of susceptibility, because near the bands of photochemical absorption the bands of thermal absorption also exist. The rule, following which the activity of light increases with its frequency, only signifies that the bands of photochemical absorption are preferentially situated in the more refrangible region of the spectrum. In the case of acetaldehyde the bands of thermal absorption extend up to the extreme ultra-violet, after which bands of photochemical absorption begin. V. Henri and Wurmser (*Compt. rend.* **156**, 230 (1913)) have studied the photochemical sensitiveness and the light absorption of acetone, acetaldehyde, and acetic acid in the ultra-violet. With acetone and acetic acid the curves of sensitiveness and absorption have their maxima nearly for the same wave-

length, and their nature is practically the same though they do not exactly coincide. Similar results have been obtained by Lasareff in his researches on the bleaching of coloured substances. The case of aldehyde has been found to be different. This substance has a maximum of absorption near 2800 Å; the maximum of photochemical susceptibility also corresponds to this region, but the absorption increases more rapidly than the susceptibility towards 2300 Å, which lies in the extreme ultra-violet. According to V. Henri and Bielecki (*Compt. rend.* **155**, 456 (1912)), the absorption band at 2800 Å is due to the aldehydic group, and the band at 2300 Å is caused by the methyl group. In the photochemical decomposition of aldehyde, with the formation of CH_4 and CO , the aldehydic group is affected, and the radiations absorbed by the methyl group are without effect. Henri and Wurmser have announced the following rule:—the photochemical susceptibility of a substance depends solely on that part of the spectrum which corresponds to the molecular grouping on which the reaction takes place. Hence one can explain why certain absorbed radiations are chemically active whilst others are simply converted into heat. Moreover it is easy to conceive also that rays of different wavelengths can produce different results in one and the same system.

In their experiments on the combination of H_2 and Cl_2 Bunsen and Roscoe stated that the absorption of light by chlorine was increased by the presence of H_2 . They believed that the light which causes a chemical reaction shows in addition to ordinary optical absorption, a photochemical extinction corresponding to the work spent in the chemical reaction. According to the measurements of Bunsen and Roscoe this energy is expected to be one-fourth of the incident radiation. The existence of this photochemical extinction should not be confounded with photochemical absorption, and has not been confirmed by subsequent work. Thus Burgess and Chapman (*J. Chem. Soc.* **89**, 1402 (1906)) could not detect any difference in the absorption of pure chlorine or its mixture with air or H_2 . Moreover Weigert (*Z. Physik* **10**, 349 (1922)) and von Halban and Siedentopf (*Z. phys. Chem.* **103**, 71 (1922)) have shown that humidity does not affect the absorption of chlorine. The experiments of Lemoine (*Compt. rend.* **118**, 525 (1894)) on the decomposition of ozone in presence of chlorine showed no evidence of the existence of photochemical extinction in these reactions. Eder believed that there is a photochemical extinction in the reduction of mercuric chloride by ammonium oxalate, but Winther (*Z. wiss. Phot.* **8**, 237 (1910)) showed that a mixture of mercuric chloride and ammonium oxalate does not show any appreciable absorption of blue rays which are photochemically active. From the above facts one can

conclude that photochemical reactions are not the result of a special kind of absorption different from ordinary optical absorption.

It can be conceived that although the existence of photochemical extinction is being denied, the distinction between the photochemical and thermal absorption is often relative, and that for one and the same substance the thermal absorption passes into the photochemical one according to experimental conditions, without change of absorption spectrum. For example, if pure chlorine is illuminated with blue light, the absorbed energy is converted into heat, the absorption is purely thermal. If the chlorine is mixed with hydrogen, although the absorption remains unchanged, the molecules which have absorbed the radiant energy become capable of reacting with hydrogen; thus the absorption becomes photochemical. Similarly, an aqueous solution of chromic acid is not altered by visible light and thus produces thermal absorption. If now oxalic acid is added to the chromic acid, the absorption in the visible spectrum remains unchanged, but the molecules of chromic acid are activated by the absorption of light and are capable of oxidizing oxalic acid. The same observations are applicable to all photochemical transformations in which two substances react according to the above scheme. The light absorbed by the photosensitive ingredient renders it chemically reactive towards the second substance, which is not sensitive to light but plays the part of an acceptor.

Lasareff (*Trans. Farad. Soc.* **21**, 475 (1925)) and Plotnikoff (*Lehrbuch der Photochemie*, Berlin 1920) suggest that in general a light sensitive substance possesses several absorption bands, of which only a part is photochemically active. The photochemical activity within each band is assumed to be proportional to the amount of light absorbed, and is independent of wavelength. The influence of different bands seems to be different. Lasareff suggests that the proportionality of a reaction-velocity to the amount of absorbed light energy is the fundamental law of photochemistry.

Plotnikoff developed expressions for the velocity of different ideal photochemical reactions on the basis that the law of mass action is applied not to the partial processes but to the integral rate of reactions.

SIMULTANEOUS ACTION OF RADIATIONS OF DIFFERENT WAVELENGTHS.

If a photosensitive system is illuminated by two rays of light having the same spectral composition, according to the law of Grotthus-Draper, their total effect is naturally the sum of their individual

effects. This simple additivity rule is expected to be valid for photochemical reactions when the two radiations have different wavelengths. It has been effectively observed by Luther and Forbes (*J. Amer. Chem. Soc.* **31**, 707 (1909)) for the oxidation of quinine by chromic acid, and by Bruner and Czarnecki (*Bull. Ac. Sc. Cracow*, 516 (1910)) in the action of bromine on toluene in presence of radiations of wavelengths 5790 Å and 5460 Å, and 4360 Å and 4050 Å. This simple additive rule has not, however, been found in other reactions.

In his researches on the addition of bromine to cinnamic acid in CCl_4 solutions, Plotnikoff (*Z. physik. Chem.* **79**, 657 (1912)) stated that the effect produced by the total radiations from a mercury lamp is much inferior to the sum of their individual effects. The simple additivity rule would be applicable to those cases where the Grotthus-Draper law is valid for all the separate radiations. Now Berthoud and Beraneck (*J. Chim. phys.* **24**, 213 (1927)) observed that this condition is not fulfilled in the above reaction, and the velocity of the reaction is proportional to the square root of the light intensity. For two active wavelengths λ_1 and λ_2 , the velocities are given by the equations: $v_1 = \sqrt{K_1 A_1}$ and $v_2 = \sqrt{K_2 A_2}$ where A_1 and A_2 represent the quantities of light absorbed and K_1 and K_2 are two proportionality factors. Now if both the radiations act simultaneously the velocity should be represented as follows: $v = \sqrt{K_1 A_1 + K_2 A_2}$. It is clear therefore that v is less than $v_1 + v_2$ and the additivity rule is not valid, because the velocity of disappearance of the active molecules increases as the square root of their concentrations. In this respect the photosynthesis of hydrobromic acid is quite similar. These relations are valid when the two active radiations are absorbed equally by the mixture under experiment; if this is not so, the relations become more complicated. In the reaction between iodine and potassium oxalate, blue and red rays are unequally absorbed, and hence the simple relations are not observed when the reaction takes place under the simultaneous action of blue and red rays.

Padoa and Miss Vita (*Gazz. Chim. ital.* **54**, 147 (1927)) have observed that the additivity rule is not applicable to the photochemical oxidation of HI by oxygen in aqueous solution. The effect of red, green, blue, and violet rays acting simultaneously is represented by 100, and the sum of the isolated rays has been found to be equal to 317. In the oxidation of oxalic acid by ferric chloride, and in the Eder reaction, the deviation has been less marked. For the first reaction the sum of the effects of blue and violet rays varies from 112 to 160, and for the second it is about 130 in place of 100, with the rays acting simultaneously.

the photosynthesis of HCl according to Padoa (*Z. physik. Chem.* **120**, 202 (1926)) — compare also Padoa and Miss Vita (*Gazzetta* **56**, 164 (1926)) — the activity of white light is higher than the calculated value according to the additivity rule, and the deviation is approximately 60 %.

The oxidation of HI by oxygen does not follow the law of Grotthus-Draper. The velocity of this reaction is proportional to the square root of the amount of absorbed energy, and thus there is deviation from the additivity rule. For the other reactions studied by Padoa the deviations are not easily explained. The law of Grotthus-Draper seems to have been verified in the photosynthesis of HCl, and in the Eder reaction. Weigert and Kummerer (*Ber.* **26**, 1207 (1913)), in their researches on the transformation of ortho-nitro-benzaldehyde to ortho-nitroso-benzoic acid, have observed that the effect of radiations of wavelength 3550 Å and 4050 Å, acting simultaneously, is greater than the value calculated according to the additivity rule. Moreover, Kuhn (*Compt. rend.* **177**, 956 (1923)) has observed that in the decomposition of ammonia the radiations acting simultaneously produce more marked effect than the value calculated according to the additivity rule. Recently Bhattacharya and Dhar (*J. Indian Chem. Soc.* **6**, 452 (1929)) have studied about 40 photochemical reactions in total light from an electric bulb, in sunlight, and in monochromatic radiations, and have found that the quantum yield is much greater in sunlight, and in the total light from an electric bulb, than in monochromatic radiations. Also the quantum yield for the hydrogen-chlorine reaction in white light is much greater than that obtained by the summed reactions of the different parts of the spectrum.

Padoa and Miss Vita (*Gazzetta* **58**, 647 (1928)) have observed that the sum of the separate actions of red, yellow, and green light is greater than the action of the corresponding amount of white light on the absorption of carbon dioxide by green plants, as measured by the amount of oxygen evolved. Intermittent white light also has a different effect from continuous light on the photochemical yield.

Recently Padoa and Miss Vita (*Gazzetta* **58**, 3 (1928)) have concluded that the sum of the photochemical effects produced by the component radiations is different from, and in general greater than, that of the resulting complex light, not only owing to variations in the intensity, but also, and in some cases solely, on account of specific effects due to variations in the frequency of the light.

On the other hand, the researches of Bhattacharya and Dhar (*Z. anorg. u. allg. Chem.* **176**, 372 (1928); *J. Indian Chem. Soc.* **6**, 143

(1929)) and Mukerji and Dhar (*J. phys. Chem.* **33**, 850 (1929)) show that the quantum yield in composite light is much greater than that in monochromatic light. Similarly, Allmand and Webb (*J. Chem. Soc.* 1518 (1929)) have shown that in the photolysis of potassium ferric oxalate, when complex light, consisting of varying proportions of two or three of the mercury lines, is used, the amount of decomposition actually observed is consistently greater by 25—30 % than that calculated on the basis of additivity. This result is the reverse of that found by Padoa and Miss Vita (*Gazzetta* **54**, 147 (1924)), working with a ferric chloride oxalic acid mixture, and using a portion of continuous spectrum. Very recently Berthoud (*J. Chim. phys.* **26**, 435 (1929)) has studied the oxidation of potassium nitrite by iodine in yellow and blue light separately, and when mixed, and has reported that the observed effect is purely additive. Berthoud has stated that in cases where the law of additivity is not obeyed, the causes are the same as those which lead to the deviation from the Grotthus-Draper law. The influence of intermittent light on the oxidation of hydriodic acid is stated to be in agreement with theory.

It appears, therefore, that the concensus of opinion is in favour of the view that the effect of composite light on a photochemical reaction is greater than that calculated on the additivity basis.

THE PHOTOCHEMICAL EFFECT IS SIMPLY PROPORTIONAL TO THE QUANTITY OF LIGHT ABSORBED.

In all the reactions of this class the variation of the velocity as a function of the light intensity and the concentration of the photo-sensitive substance, can be expressed by a general formula which can be deduced from the laws of Grotthus-Draper, Lambert, and Beer relating to light absorption. If dx is the diminution of the concentration of the photosensitive substance in time dt , the quantity of matter transformed in unit time in the total volume V is given by the relation

$$\frac{V dx}{dt} = KA. \quad (1)$$

V being equal to Sl and $A = S(I_0 - I_l)$, the velocity of the reaction, i.e. the quantity of matter transformed in unit time and in unit volume, is expressed by the following relation:

$$\frac{dx}{dt} = K \frac{(I_0 - I_l)}{l}. \quad (2)$$

After a time t , the concentration of the absorbing substance becomes equal to $(a - x)$. Hence

$$I_0 - I_t = I_0[1 - e^{-k(a-x)}]. \quad (3)$$

By substituting for $(I_0 - I_t)$ in equation (2), the following relation is obtained:

$$\frac{dx}{dt} = K \frac{I_0}{l} [1 - e^{-k(a-x)}]. \quad (4)$$

This general relation is simplified in the two important cases where the absorption of light is either complete or very feeble.

1. *Absorption is complete*: — When this condition is realized, the term I_t is negligible and the general formula (4) becomes:

$$\frac{dx}{dt} = K \frac{I_0}{l}. \quad (5)$$

The velocity of the reaction is thus proportional directly to the light intensity, inversely proportional to the thickness of the cube (the reaction vessel), and independent of concentration. Hence the order of such a reaction is zero. If the light intensity is constant, the velocity is constant as long as the absorption is complete, and the quantity of matter transformed in the total volume V is expressed as follows:

$$Vx = KSI_0t. \quad (6)$$

This relation is simply a linear function of time.

The total quantity of matter Vx transformed does not depend on the agitation of the reacting solutions; but if the solutions are not agitated they become heterogeneous. The photochemical reaction takes place only in the region where absorption of light occurs. As the absorbing substance is used up, the light rays penetrate more profoundly, and the zone of reaction is shifted from the surface to the interior of the liquid. If the reaction products are colourless one can follow the progress of the reaction by observing the shift of the limit between the decolorized and the unchanged regions. This limit is naturally more clear when the initial mixture is highly coloured. The concentration of the absorbing photosensitive substance being equal to a , a shift, $S\Delta l$, of the border of the coloured zone corresponds to the quantity of matter transformed $= Sa\Delta l$; and according to equation (6) it is equal to KSI_0t , hence

$$\Delta l = K \frac{I_0}{a} \cdot t.$$

This equation has been verified by Benrath and Schaffganz (*Z. physik. Chem.* **103**, 139 (1922)) in the reduction of FeCl_3 by tartaric acid in silicic acid jelly, which is used for stopping convection currents. It is clear that this relation would not be valid if the reactions were not directly proportional to the quantity of absorbed light.

2. Absorption is feeble: — When the absorption is feeble, equation (4) breaks down, by putting $il(a-x)$ for $[1 - e^{-il(a-x)}]$ (see p. 17) to: —

$$\frac{dx}{dt} = KI_0 i(a-x) = K_1(a-x),$$

and on integration, we get the following

$$K_1 = KI_0 i = \frac{1}{t} \log_e \frac{a}{a-x}, \quad (7)$$

or
$$K_1 = \frac{1}{t_2 - t_1} \log_e \left(\frac{a - x_1}{a - x_2} \right),$$

where x_1 and x_2 are the amounts transformed at times t_1 and t_2 respectively. This equation differs from the unimolecular thermal equation only in the value of K , which is not constant in the photochemical reaction but varies with the intensity of the light.

3. Absorption is neither feeble nor complete: — In this case the velocity is expressed by equation (4), which on integration becomes:

$$KI_0 i = \frac{il(x_2 - x_1) + \log_e \frac{1 - e^{-il(a-x_1)}}{1 - e^{-il(a-x_2)}}}{t_2 - t_1}.$$

When the absorption is practically complete the exponents, $il(a-x)$, are large, and the terms $e^{-il(a-x)}$ are negligible. The above formula reduces to equation (7) when the absorption is sufficiently feeble.

It seems probable that photochemical reactions of which the velocity is determined solely by the law of Grotthus-Draper are relatively common. However, the above formulae have rarely been completely experimentally verified.

Wittwer stated that the photochemical decomposition of chlorine water is unimolecular; but his conclusion appears to be erroneous. In reality, subsequent researches have shown that the results of Wittwer are not correct, and the reaction is more complicated than he supposed.

Bunsen and Roscoe observed that hydrochloric acid retards the photochemical decomposition of chlorine water. Benrath and Schaffganz (*Z. physik. Chem.* **103**, 139 (1922)) stated that HClO is an intermediate product in the decomposition of chlorine water. Consequently the reaction is of a complicated nature.

Amongst the reactions in which a proportionality between the light absorbed and the photochemical effect exists are the following: — 1) decolorization of dyestuffs (Lasareff). 2) The velocity of the oxidation of quinine by chromic acid is proportional to the quantity of light absorbed by the quinine, but the reaction appears to be complicated. 3) The photochemical decomposition of laevulose, investigated by Berthelot and Gaudechon (*Compt. rend.* **156**, 707 (1913)), takes place under the influence of ultra-violet rays ($< 4000 \text{ \AA}$). The velocity of this reaction can be measured by the volume of the gas, which consists mainly of CO . The velocity increases with the concentration in the same proportion as the amount of light is increased. The reaction is of the first order when the concentration is very small, and the order becomes zero when the absorption is complete. 4) The decomposition of hypochlorous acid is stated by Clark and Iseley (*J. Ind. Eng. Chem.* **12**, 1116 (1920)) to be unimolecular when the absorption is feeble. 5) According to Rideal and Norrish (*Proc. Roy. Soc.* **103**, 366 (1923)) the photochemical decomposition of potassium permanganate appears to be unimolecular in ultra-violet radiations of wavelength 3100 \AA . 6) The decomposition of NOCl is stated by Kiss (*Rec. trav. chim.* **42**, 665 (1925)) to be unimolecular in white light. 7) Bredig and A. von Goldberger (*Z. physik. Chem.* **110**, 521 (1921)) have observed that in the photochemical decomposition of formaldehyde in the gaseous state, in radiations of wavelength 3600 \AA , with formation mainly of CO_2 and H_2 , the order is zero when the pressure is high, and unity when the pressure is low. 8) The photochemical decomposition of ammonia in ultra-violet light also belongs to this group. Recently, numerous photochemical reactions have been investigated by Dhar and his collaborators, and most of the reactions investigated by them are unimolecular in the dark as well as in presence of light. Thus the reactions between chromic acid and oxalic, tartaric, and lactic acids are unimolecular with respect to chromic acid in sunlight, as well as in the radiations of wavelengths 4725 , 5650 , 7304 \AA , whilst the reaction between chromic and citric acids appears to be semimolecular in sunlight and unimolecular in the other radiations.

We have also observed that photochemical reactions of the following substances are *unimolecular*:

Oxalic acid and chlorine; potassium oxalate and bromine; rochelle salt and bromine; methyl alcohol and bromine; ethyl alcohol and bromine; propyl alcohol and bromine; isopropyl alcohol and bromine; butyl alcohol and bromine; sodium tartrate and iodine; sodium lactate and iodine; sodium malonate and iodine; hydroxylamine hydrochloride and iodine; hydrazine hydrochloride and iodine; oxidation of neocyanin; oxidation of dicyanin; mercuric chloride and ammonium oxalate; potassium persulphate and potassium iodide; quinine and chromic acid; oxalic acid and potassium permanganate; tartaric acid and potassium permanganate; citric acid and permanganate; lactic acid and permanganate; hydrolysis of cane sugar; decompositions of trichloroacetic acid and ferric thiocyanate. In all the above cases the absorption of light is feeble.

Photochemical reactions between the following pairs of substances have been found to be semimolecular:

Potassium oxalate and iodine; sodium formate and iodine; sodium citrate and iodine; sodium malate and iodine; ferrous sulphate and iodine; sodium nitrite and iodine; whilst the following have been found to be zero-molecular:

Acetone and iodine; oxidation of iodoform; iodic acid and oxalic acid; decomposition of potassium persulphate. Very recently we have shown that the decompositions of sodium cobaltinitrite and potassium cobaltioxalate are unimolecular in total light from a 1000 watt gas-filled tungsten-filament lamp; whilst the same reactions become zero-molecular in sunlight, which is highly absorbed.

An influence of concentration on the photochemical effect, independent of that which results directly from variation of light absorption, is observed in certain reactions where a single substance is transformed, but generally in those reactions which take place between different substances. The opinion has been held by certain authors that in all photochemical reactions between two substances, one of which is photosensitive, the velocity can be expressed by the same general formula. This view is not in accordance with experimental facts. The velocity expression, however, changes in form when one passes from one reaction to another, sometimes even with reactions of similar type, e.g. photosynthesis of HCl and HBr. Thus we have to investigate each reaction separately.

CHAPTER III.

Light Sources.

Forbes (*J. Phys. Chem.* **32**, 482 (1928)) states: "The ideal photochemical light source is extremely intense and concentrated, and should be efficient, convenient, and economical... A concave mirror behind the source, or a projection apparatus increases the intensity of illumination. A weak or unsuitable source takes such heavy toll in time spent and in quality of results, that economy is the worst form of extravagance.

"*Sunlight* costs nothing and is extremely intense in the visible part of the spectrum, especially at high altitudes or in the tropics. Its spectrum is for photochemical purposes best imitated by the blue gas-filled tungsten lamp, or by the snow white flame arc. Combinations of the mercury vapour lamp with various thermal radiators are its equivalent for colour matching only. The mercury vapour lamp with a crown glass filter is said to behave like sunlight in fading tests. Lenses or concave mirrors concentrate sunlight further, and water filters mitigate the thermal effect. The extreme variability of sunlight, the need of a heliostat, and the fact that its spectrum is continuous, except for the dark lines, all handicap quantitative monochromatic work. Such drawbacks, however, must not discourage further investigation of its immense possibilities." The utilizable energy on the surface of the earth is almost entirely due to sunlight. The sun consists of a white hot radiating surface called the photosphere, which is surrounded by layers of vapours at a lower temperature, called the chromosphere. The light emitted by the photosphere is continuous in character but the observed spectrum consists of a continuous radiation crossed by a very large number of fine dark lines (Fraunhofer lines) due to the absorption of light by elements existing in the chromosphere. The spectrum of sunlight as observed on the earth's surface extends from approximately 2900 Å—30,000 Å. Hence sunlight contains ultra-violet rays extending from 2900 Å to 3800 Å, visible light from 3800 Å to 7500 Å and infra-red from 7500 Å to 30,000 Å. The position of maximum energy occurs within the visible spectrum. In the case of an electric arc or incandescent filament lamp the maximum is shifted into the short infra-red region.

At the present time a great deal of interest is being shown in the ultra-violet portion of the solar spectrum, since rickets are associated with its absence from sunlight. In the north temperate zone rickets are commonly found in the late winter and early spring. This disease decreases in summer, and the phenomenon has been assumed to be associated with seasonal variations in sunlight. Schall (*Chem. Zeitung* **34**, 267 (1910)) has reported that paper impregnated with p-phenylene diamine nitrate becomes blue when exposed to radiations shorter than 3130 Å. As the solar spectrum is assumed to end at 2950 Å, the paper is suitable for determining the variations of the solar radiation of short wavelengths (compare Mott and Bedford. *J. Ind. Eng. Chem.* **8**, 1029 (1916)).

Recently Walsh (*J. Sci. Instr.* **5**, 81 (1928)) has discussed the uses of artificial daylight and means for its production. The only practical method of producing artificial daylight is the subtractive method, in which the excess of red and yellow light is removed by an absorbing screen or by reflection from a coloured surface. Its production is therefore less efficient than that of ordinary artificial light.

At present the only means by which solar energy is utilized is in the photosynthesis taking place in the green plants. The active rays seem to be those absorbed by chlorophyll, and it is interesting to note that photosynthesis utilizes those rays which are most intense in the solar spectrum.

Animal life depends for its existence on the photochemical processes occurring in the living plant, but unfortunately this change is not clearly understood, although numerous workers are tackling the problem.

ELECTRIC LAMPS.

Forbes (*loc. cit.*) states: "Incandescent filaments, straight or coiled, should, if used with a monochromator, approximate to the dimensions of the slit. The thin glass bulb transmits much ultra-violet light, and a quartz window can be added. Overloading greatly increases the ultra-violet output, though shortening the life of the lamp. The Nernst glower is still made by the Glasco Lamper Gesellschaft, Berlin; a laboratory recipe has been published; its spectrum is very faint beyond 2500 Å. 'Glowbar' is useful for infra-red work only. If magnesium could be fed uniformly into oxygen over a considerable period, it would be of greater value."

The incandescent carbon filament lamp rarely attained 2000° and its light was intermediate in whiteness between that of a gas

mantle and an oil lamp. The replacement of carbon by metals such as tantalum and tungsten, which can be raised to a much higher temperature than carbon, was a great improvement. The tungsten filament lamps give out a whiter light than most illuminants, usually last about 1000 burning hours, and give about 0.65 candle per watt. Most lamps show an increase of about 4 per cent in candle power for every 10 per cent increase in the voltage used. Since the current only increases at a rate which is half of the rate of increase in voltage, an increase in voltage means twice as great a percentage increase in candle power per watt. However, it should be emphasized that even one percent increase in voltage may result in a shortening of the life of the lamp by 15%. The temperature to which a tungsten filament can be raised without appreciable volatilization can be considerably increased if the bulb is filled with an inert gas such as argon or nitrogen at about atmospheric pressure. The gas-filled lamp gives about 1.2 candles per watt.

For projection work, and experiments requiring a point source of light showing a continuous spectrum in the visible, the pointolite lamp is of great value. In the pointolite lamp a solid lump of tungsten metal acts as the positive electrode. It becomes incandescent as a result of bombardment by a stream of electrons from a negative tungsten plate, while a small tungsten filament covered with refractory oxides acts as the starter for the lamp. The first effect is the emission of electrons from this filament, and thus the space between the plate and the positive electrode is ionized. Once the lamp is started the auxiliary small filament is switched out of the circuit.

Flames of burning gases are rarely used in photochemical work. A considerable amount of ultra-violet light is emitted by acetylene properly burnt in oxygen.

Lamps depending on the principle of burning liquids in oxygen find very little application. The Wulf carbon disulphide lamp burning in oxygen (Wulf, *Ann. Physik. iv*, **9**, 946 (1902)), which yields light fairly rich in ultra-violet rays, has sometimes been used. Wulf investigated various sources of ultra-violet rays, and discarded the Nernst lamp because it gave out little ultra-violet radiation, and the carbon arc because of its fluctuating nature. Wulf has constructed a lamp in which carbon disulphide and oxygen are supplied through brass tubes to the mouth of a burner, above which is suspended a small copper ball to cause a rapid admixture of oxygen and carbon disulphide vapour. An intense white light is produced by a flame 20 to 30 cms. in height. A metal chimney placed slightly above the base of the flame cuts off the

upper fluctuating portion of the flame and thus yield a fairly constant source of light. Care should be taken that the carbon disulphide and oxygen do not mix until the desired point of combustion is reached. As carbon disulphide is a very inflammable and explosive substance, the production of ultra-violet radiations in this manner is not without danger.

In order to get ultra-violet radiations, Tassilly and Gambier (*Compt. rend.* **151**, 342 (1910)) have burnt carbon disulphide in nitric oxide.

For certain purposes the high tension disruptive spark discharge between electrodes of metals like aluminium, cadmium, copper, cobalt, iron, nickel, magnesium, tin, lead, tungsten, brass, and zinc has been utilized. The aluminium spark, working under water, forms a very useful, though feeble, source of continuous ultra-violet radiation. Howe (*Phys. Rev.* (2), **8**, 674 (1916)) has described a fine source of continuous radiation from tungsten electrodes sparking under water, whilst Fulweiler and Barnes (*Journ. Franklin Inst.* **194**, 83 (1922)) obtained a good source of ultra-violet light showing a continuous spectrum in the following manner: — Tungsten rods 3.5 mm. in diameter were mounted in brass rods which screwed into solid rubber stoppers. These were fitted into a pyrex bulb of about 500 c.c. capacity. The electric circuit requires a transformer of X-ray type, two condensers, and an auxiliary spark gap in series with the tungsten spark, which is about 2 cms. under water. The auxiliary electrode runs most smoothly with an air blast between the electrodes. These sources are more valuable for photographic work on absorption spectra than for photochemical reactions.

The open arc between carbon or metal electrodes forms a specially useful light source of fairly constant intensity. In order to obtain good results, it is only necessary to connect a pair of electrodes, which may be of the same or different metals, to a supply of direct-current and run the arc at 220 volts and 5 amperes. More intense light can be secured with higher current consumption. With iron or iron and nickel electrodes in air the spectrum extends in air from 2100—8500 Å, and consists of fine closely packed lines. Arcs between metallic poles cannot be successfully run by alternating current. With carbon electrodes the spectrum is continuous, and extends into the ultra-violet up to 2800 Å. When the positive carbon is cored, and has a centre of iron, and is used in conjunction with a negative electrode of solid carbon, the spectrum extends further into the ultra-violet. When carbon electrodes are soaked in aqueous solutions of various salts such as potassium silicate, potassium carbonate, fluorides, and salts which on gentle ignition leave oxides,

rare earth salts, magnesium and zinc salts, the light approaches sunlight.

A specially prepared carbon arc which is used in actinotherapy is described as having in its centre a complex mixture of rare earth oxides and fluorides obtained as a by-product in the gas mantle industry. The mixture contains cerium, lanthanum, neodymium and praseodymium. Mott and Bedford (*J. Ind. Eng. Chem.* **8**, 1029 (1916)) and Moore (*Trans. Amer. Electrochem. Soc.* **27**, 435 (1915)) found that the flaming white carbon arc greatly excelled all other light sources tried for the photo-chlorination of methane.

Flame carbons treated with: —

- (I) Calcium fluoride give a yellow light deficient in blue.
- (II) Strontium fluoride, a red light.
- (III) Copper salt, a blue light.
- (IV) Silicon or iron salts, reddish violet.
- (V) Lanthanum oxide, pure white.
- (VI) Titanium salts, blue.
- (VII) Didymium oxide, pure violet.
- (VIII) Thorium oxide, reddish.
- (IX) Ceric oxide, pure blue.

Piutti (*Atti R. Accad. Lincei* (v) **22**, ii (92) (1913)) has stated that carbon electrodes, which have been alternately heated to redness and immersed in ferric chloride solution, may be employed with advantage instead of iron electrodes for obtaining ultra-violet rays.

Warm (*Z. wiss. Phot.* **25**, 365 (1928)) has described a light source devised by Auer von Welsbach, consisting of a spark between two electrodes which alternately touch and separate as a result of the effect of an interrupted electromagnet. This source gives both arc and spark lines, and a continuous passage from one type to the other can be made by increasing the current.

Forbes states: "The ordinary carbon arc spectrum is weak beyond 2500 Å. The spectral energy distributions in crater and flame are unlike, and the lines are disadvantageously spaced. Basset (*Trans. Amer. Electrochem. Soc.* **44**, 153 (1923)) has studied carbon arcs carrying several hundred amperes. The flaming arc has been carefully studied especially by Mott (*Trans. Amer. Electrochem. Soc.* **31**, 365 (1917); **37**, 665 (1920)). Of many metals, copper, cadmium, iron, and tungsten are most frequently employed as electrodes. King (*Astrophys. J.* **62**, 238 (1925); *Science* **65**, January 7, Supplement 10 (1927)) has operated arcs between metallic rods with 1000—2000 amperes, producing normal

and enhanced spectra of great intensity. The copper arc of Meyer and Wood (*Phil. Mag.* **30**, 449 (1915)) gives radiations of very short wavelengths. W. Taylor (*Phil. Mag.* **49**, 1166 (1925)) found the "Pointolite lamp very intense in the visible."

"Sparks between metallic electrodes are almost indispensable for work below 2500 Å. Warburg's zinc sparks (*Z. Elektrochem.* **27**, 133 (1921)) gave at 2540 Å a thousand-fold the intensity of his mercury vapour lamp. The elements of the second and third groups give advantageous spacing of lines. Many papers on the subject have accumulated, but more data on absolute spectral intensities under specified conditions would be welcomed by photochemists. Warburg, Lenard and Ramsauea, and others, have described adequate installations. Many such outfits are underpowered. A transformer consuming several kilowatts and yielding at least 20,000 volts should be used. Special wiring may have to be run through the building. Mica condensers are better than Leyden jars. Warburg housed his spark in a chamber with a quartz window and an airblast. He threw its image on a screen and kept it constant by a feed worked by a glass rod, but the intensity varied 3—6%. Harrison and Hesthal combatted unsteadiness by rotating the lower electrode, and by regulating the gap and the primary impedance. Kowalski, by adjusting the capacity, brought the greatest intensities into the middle ultra-violet."

MERCURY VAPOUR LAMPS.

The first attempts at the making of mercury lamps failed owing to the increase in the electrical resistance as the pressure of the vapour of mercury became greater. For satisfactory working of the lamp, the mercury vapour should be condensed at the same rate as fresh mercury volatilizes. By determining the vapour resistance Cooper-Hewitt devised, in 1901, a lamp in which the mercury was cooled and condensed at about the same speed as it vapourized.

The next step in the improvement of mercury lamps was taken by Arnos in 1902, who showed that a mercury arc could be obtained by passing direct current through an evacuated tube containing vapour of mercury. As a light source, the glass mercury vapour lamp suffers from the disadvantage of emitting a very green light, whilst as a source of ultra-violet light, its use is restricted by the poor transmitting power of glass. The advent of transparent fused quartz immediately established the quartz mercury vapour lamp in the forefront as a suitable source of ultra-violet light. These lamps behave very satisfactorily

in many respects, and are largely used by photochemists. Numerous modifications have been described. The cathode is always of mercury, the anode of mercury or of tungsten. In the latter case reversal of polarity must be avoided. The commercial lamps have sealed-in electrodes and some of them can be worked in both horizontal and vertical positions.

With the object of carrying out investigations in the extreme ultra-violet, Wolff (*Ann. Physik* (IV), **42**, 825 (1913)) used a quartz lamp of the Stark and Küch pattern (*Phys. Zeitschr.* **6**, 438, (1905)) made by Heraeus.

Fischer (*Ber.* **38**, 2630 (1905)) described a mercury arc lamp suitable for chemical purposes, which he used in the experiments on the formation of ozone. A form of quartz mercury lamp suitable for bacteriological work has been described by Knipp (*Phys. Rev.* **30**, 641, (1910)). Tian (*Compt. rend.* **156**, 1063, (1913)) has adopted a lamp made of transparent quartz, at the centre of which an insulated iron wire passes, thus making contact with the drop of mercury at the bottom which forms the cathode. The anode is a small iron cylinder. This type of lamp can be operated at low voltage, and is of convenient shape for immersion in liquids.

A type of arc lamp using a mercury cathode and tungsten anode has been recommended by Urbain, Scal, and Feige (*Compt. rend.* **152**, 255 (1911)). Tungsten is used because of its high melting point, and it is necessary to work the lamp in a vacuum or in an inert gas, because when the smallest trace of oxygen is present the walls of the enclosing vessel become darkened by the production of oxides. A mercury vapour lamp with a carbon anode and a mercury cathode has been prepared by the General Electric Company.

For exposing gases to ultra-violet radiations, different types of mercury vapour lamps have been recommended by Chapman, Chadwick, and Ramsbottom (*J. Chem. Soc.* **91**, 945, (1907)), Coehn and Becker (*Z. phys. Chem.* **70**, 90 (1910), and Weigert (*ibid.* **80**, 69 (1912)). The introduction of the mercury lamp into spectroscopy and polarimetry has been recommended by Lowry (*Trans. Farad. Soc.* **7**, 267 (1912)); Bovie (*J. Amer. Chem. Soc.* **37**, 1721 (1915)) has described a mercury lamp in which the principle of the mercury air pump has been incorporated into the design.

Weigert (*Z. physik. Chem.* **80**, 67 (1912)) pointed out that the quantitative study of photochemical gas reactions under the influence of ultra-violet radiation is rendered difficult by the increase of temperature when the lamp is working. If we try to avoid this heating, by

water cooling, the radiation has to pass through a layer of water where it is largely absorbed. Henri (*Compt. rend.* **153**, 426 (1911)) showed that the radiation becomes more intense as the temperature of the luminous tube becomes greater. By cooling with water, the radiation becomes 14 times less powerful than with air with the same amount of electricity used up. Thompson (*British Patent* 28757, December 20 (1911)) recommends that for the purpose of sterilizing water and other liquids, the vapour pressure in the mercury lamp be kept as low as possible. Perkin (*Trans. Faraday Soc.* 199 (1918)) has described a lamp which is constructed of fused quartz, and so arranged that gases can be circulated through it. Ultra-violet lamps containing argon, helium, and neon have been used by Bayle, Fabre, and George (*Bull. Soc. Chim.* (4), **37**, 89 (1925)). The Quartz Lamp Co., Hanau, has described a double walled mercury vapour lamp suitable for medicinal purposes, for the sterilization of milk and water, and in the preparation of patent leather and artificial rubber.

The mercury vapour lamps which are largely sold in the market at the present time are of two main types:—those having a mercury anode and those having a tungsten (or other metal) anode. The first type of lamp is built along the lines of the Heraeus lamps, and the electrical connections are made by ground-in pins of invar, an alloy possessing nearly the same coefficient of expansion as quartz. The tungsten anode type is usually prepared with sealed-in connections, and a graded glass-quartz seal is used to relieve the strain due to differences in expansion. For the mercury anode lamp, longer life and greater ease of repair have been claimed, whilst the tungsten anode lamps have the advantages of greater facility of manufacture, mechanical simplicity, and ease of adaptation for working in a vertical position. The manufacturers supply detailed directions for operation. The ultra-violet radiations are so intense that the air becomes immediately charged with ozone.

The mercury vapour lamp recently invented by Foulke (*New York Regional meeting of the A. I. E. E.* No. 11 (1926)) appears to have immense possibilities for photochemical operations. There are no electrodes, but the vapour is excited by a rapidly changing electromagnetic field. The light intensity is greatly increased by small amounts of inert gas.

Quartz mercury vapour lamps yield for a limited period a very constant source of ultra-violet rays, and one in which the radiation is definite when the voltage, amperage, and length of the tube are known. The spectrum of the quartz mercury vapour lamp extends from 1850 to

14,000 Å. The radiations of longer wavelengths are largely concentrated in the yellow green lines 5764 and 5791 Å and the green line 5461 Å. Hence the visible portion of the spectrum of a mercury lamp is of great value as a source of high intensity monochromatic light for polarimetric, spectroscopic, and interferometer operations. The radiations of wavelengths less than 4500 Å represent two thirds of the total radiations of wavelengths less than 14,000 Å. The ultra-violet radiation is also concentrated in a few lines of high intensity. The specially strong lines are a pair at 3650—3654 Å, 3984 Å, and a pair at 4046—4078 Å.

Coblentz, Long, and Kahler (*J. Franklin Inst.* **187**, 112 (1919)) quantitatively measured by means of a thermopile the decrease in intensity of emission with use of a mercury lamp, although D. Berthelot and H. Gaudechon observed in 1912 (*Travaux scientifiques de D. Berthelot*, Paris (1917)) the deterioration of a mercury lamp with time, towards the photochemical decomposition of laevulose. It was reported by Coblentz, Long, and Kahler that the intensity of the total radiation, as well as the ultra-violet component, decreased to one-half to one-third of its initial value in 1000 to 1500 hours. During the first 500 hours' use no appreciable difference was observed in the proportion of ultra-violet light emitted.

Nelson (*Proc. Amer. Soc. Testing Materials* **22**, 485 (1923)) investigated the deterioration of a mercury vapour lamp by its ionizing influence on a charged zinc plate, and only radiations shorter than 3000 Å are concerned in this effect. No decrease was noticed after 500 hours' use, but after 1800 hours the emission had fallen to about 50%. Courmont and Nogier (*Illuminating Engineer London*, **4**, 503 (1911) and Le Bon (*Compt. rend.* **153**, 49 (1911)) suggested that the diminution in the ultra-violet radiation from an old quartz mercury vapour lamp is probably caused by a coating of greyish substance. Courmont and Nogier declare that, if it is desired to preserve a constant efficiency of ultra-violet radiation from the mercury vapour lamp, the temperature of the quartz must be kept low. The average life of a 220 volt mercury lamp varies from 2500 to 3000 hours, when properly handled. The deteriorated lamp can be improved by re-exhaustion, which can be repeated three times with ordinary lamps. Others recommend that after deterioration, the stopper be taken out and the mercury carefully removed. The whole lamp is then cleaned and dried. If the quartz tube has become discoloured, it should be heated to redness so that the quartz may recover its transparency. Some manufacturers claim to be able to repair old lamps completely.

VAPOUR LAMPS OF OTHER METALS.

Stark and Küch (*Physikal. Zeitschr.* **6**, 438 (1905)) worked with Heraeus quartz lamps with electrodes of melted cadmium, zinc, lead, bismuth, antimony, tellurium, and selenium. Most of these lamps are of little practical value because of the difficulty of starting them, although the antimony and cadmium vapour lamps are easier to start than the zinc and the lead lamps. The starting of the lamps is effected by a spark from an induction coil, and the metal is heated by a gas blast lamp until sufficient metallic vapours are produced to form an arc. The bismuth lamp requires intense heating, burns at 3 amperes, and does not require water cooling unless a very strong current is used. The spectrum covers a very wide range, so that substances when illuminated by an antimony vapour lamp more nearly resemble their normal daylight colour than when mercury or some other metallic arcs are used. The antimony vapour lamp causes very strong fluorescent effects, and sodium glass fluoresces with a greenish yellow colour, while lead glass shows a blue fluorescence.

Lowry (*Trans. Faraday Soc.* **7**, 267 (1911)) devised a lamp of two electrodes of a cadmium silver alloy for polarimetric work. On striking an arc between the electrodes, a brilliant spectrum is emitted including the lines of silver and cadmium. Lowry and Abram (*ibid.* **10**, 103 (1915)) have used a lamp, in which the arc is maintained between water cooled electrodes of solid cadmium. This is a useful lamp, partly because there is little vaporization, but mainly because the danger of cracking the silica tube, when the lamp is started or stopped which characterizes the molten metal lamps, is entirely avoided. The chief difficulty in the manufacture of metallic vapour lamps is the danger of the quartz cracking whenever the lamp is started or stopped. The reason of this is the unequal expansion and contraction of metal and quartz, and little progress can be achieved unless the problem of a satisfactory metal to quartz seal is solved.

Sand (*Proc. Phys. Soc.* **27**, 127 (1914)); **28**, 94, (1915)) noted that molten metallic lead, when solidified in contact with glass, will form an air-tight joint with the latter, and these joints can stand changes of temperature without cracking. With quartz the joints are usually made inside a tube in conjunction with a tungsten or molybdenum wire seal. Sand applied this idea to the construction of a cadmium vapour lamp running at a high temperature, the metal being melted by a Bunsen burner before starting, so that the arc could be struck by tilting. Once it is started, the lamp rapidly becomes hot enough to keep the metal in

the molten condition. The main difficulty in this lamp is the removal of the dissolved gases and oxide from cadmium, and in preventing it from adhering to the glass, so as to avoid the cracking of the silica tube on heating and cooling. This adherence of the metal to the glass is avoided by the addition of zirconium oxide powder, obtained by the ignition of zirconium nitrate. Bates (*Phil. Mag.* (VI), **39**, 353 (1920)) attempted to construct cadmium vapour lamps by the addition of gallium to cadmium; the alloy of cadmium and gallium is so soft that no cracking is possible.

Amalgams containing cadmium, zinc, thallium, caesium, and an alloy of sodium and potassium have been used, but the results are unsatisfactory, because the added metal collects at one pole or on the walls, and constant light is not obtainable. The Bates lamp appears to be the most intense and steady of this group. According to Burgess of the Bureau of Standards, all the cadmium lines in the region 2500 to 1850 Å can be obtained from the Bates lamp with greater intensity than from any other source.

Precautions are necessary when working with ultra-violet light, and high grade goggles with sides must be worn near a powerful source. When there is no lateral exposure, ordinary spectacles afford some protection. The safest protective glasses are so dark, either red or green, that it is practically impossible to see any thing clearly when wearing them in daylight. With quartz mercury vapour lamps or arcs the light is, however, quite intense enough for satisfactory working.

TRANSPARENCY OF DIFFERENT SUBSTANCES; AND LIGHT FILTERS.

The monochromatic constituents of a source of light can be separated by a spectroscope, but colour screens are more convenient and have the advantage that they permit us to utilize the entire source. The transparency of glasses and other materials can only be determined satisfactorily by spectrophotometry. Ordinary varieties of glass possess a slight green tinge due to the presence of ferrous salt, and the spectral transmission of such a glass is approximately complementary to that of a glass containing a little manganese. The green tinge of glass due to iron salt is neutralised by adding a little manganese dioxide to the melt of glass, but this glass transmits less than the iron glass or the manganese glass, which becomes purple on long exposure to light or X-rays. This colouration disappears under moderate heat from a Bunsen burner. Potash glasses free from manganese become bluish and soda glasses yellowish green on long exposure to light or X-rays. Because

of the magnitude of the loss in transmission which occurs in some glasses when exposed to solar or ultra-violet radiations, it would be better to tolerate the slightly greenish tinge of ordinary glass. For outdoor illumination the use of manganese in glass would be unsatisfactory. According to Luckiesh (*J. Franklin Inst.* **186**, 111 (1918)) the addition of a very small amount of cobalt salt to a lead soda glass increases the ultra-violet transmission to a small amount. Hence it appears that accurate spectroscopic data are necessary for ascertaining the light absorption of different types of glass, and visual observation is practically useless.

Coblentz (*J. Franklin Institute* **188**, 255 (1920)) investigated the absorption of various commercial protective glasses and reported that red glass absorbs the ultra-violet, most of the visible rays, and practically no more of the infra-red than clear glass. Amber glass absorbs the ultra-violet and some of the visible spectrum. Green glass is opaque to ultra-violet and has a wide absorption at about 10,000 Å. Blue glass transmits ultra-violet but absorbs in the visible spectrum. Blue green absorbs the ultra-violet and infra-red. Black glass does not give sufficient protection when the operation is carried on near a source of intense ultra-violet, but absorbs strongly in the visible spectrum. Any glass which transmits beyond 3500 Å at 1 mm. thickness should be rejected. For operation with feeble lights containing much ultra-violet radiation, thick orange glasses are recommended. A thin film of gold absorbs the infra-red and ultra-violet, and to some extent the visible rays depending largely upon the thickness of the film.

Crookes (*Phil. Trans. A.* **214**, 1 (1914)) prepared glasses which cut off more than 90% of the heat radiation, are opaque to the invisible ultra-violet rays, and have a scarcely noticeable colour when used as spectacles. The ideal glass, which can transmit all the colours of the visible spectrum, and cuts off the invisible rays at the ultra-violet and infra-red ends of the spectrum, has not been obtained. The Corning Glass Works prepared in the following way certain types of glasses for absorbing ultra-violet radiations: — To an ordinary lime, barium, lead, or zinc glass, add (A) 6% titanium dioxide, and nitre in sufficient quantity to prevent the reduction of the titanium dioxide, with or without cerium oxide or vanadium oxide, or (B) 1% of a higher oxide of vanadium than V_2O_5 , with or without nitre, and a complementary but inert substance from the absorption point of view (manganese dioxide, cobalt, nickel or uranium oxide) to change the colour of the glass from green to amber. The effectiveness of titanium oxide is half of that of cerium oxide. A soda lime glass containing 7.7%

titanium dioxide and 7.7% cerium nitrate looks quite clear, with a yellow tinge, and plates of two millimeters thickness completely cut off the 3650 Å line. A glass containing both cerium nitrate and titanium dioxide has a more brilliant colour, and shows a better absorption than a glass containing one of these substances superimposed on a glass containing the other. The addition of borax increases the refractive index of glasses containing titanium dioxide. Conversion of the higher oxides of vanadium to V_2O_3 should be prevented, because the latter does not cut off the ultra-violet rays. Addition of nickel oxide makes a glass very suitable for the transmission of ultra-violet, and the cutting off of visible and infra-red radiations. A large proportion of borax in glass containing vanadium oxide completely cuts off the ultra-violet line 3650 Å in plates of 4 millimeters thickness. According to Taylor (*U. S. Patent 1,292,147 and 1,292,148*) glass for absorbing ultra-violet rays is made with titanium oxide as an essential constituent, and consists of sand 49—60 parts, soda 22—25, nitre 4.6—5.2, calcium carbonate 0—6, titanium oxide 4.25—8, cerium nitrate 0—7.7, vanadium oxide 0—0.35, borax 0.67—1, and arsenious oxide 0.4 to 0.5 parts. Glass of this composition possesses a clear brilliant yellow or yellowish green colour suitable for optical purposes. Taylor (*U. S. Patent 1,414,715 May 2, (1922)*) has prepared a flesh coloured glass of high ultra-violet absorption, and good visible transmission, by using 3.6% cerium dioxide and 0.2% manganese dioxide with silica, potash, soda, and lime. Less than one per cent of the rays of wavelengths shorter than 3350 Å are transmitted by a glass of the following composition: — SiO_2 , 70%; K_2O , 8%; Na_2O , 11.8%; CoO , 5.5%; CeO_2 , 4.5%; and MnO_2 , 0.2%.

The relative efficiency of various types of glasses and of various thicknesses, has been investigated by Voegelé (*Illuminating Engineer*, London 2, 543 (1909)) by photographing the spectra of a Heraeus quartz mercury vapour lamp through these glasses of various thicknesses.

In the following table the transparencies of various materials are recorded:

Substance	Limit of transparency
Flint glass, 2 mm. thick	2750 Å
„ „ 1 mm. „	3150 Å
Crown glass	2950 Å
Mica 0.5 mm. thick	2800 Å
Uviol glass 1.3 mm. thick	2530 Å
Vita glass 1.3 mm. thick	2750 Å
Pure water	2000 Å
Quartz 5—10 cms.	1800 Å
Fluorspar 1 mm.	1200—1300 Å

Substance	Limit of transparency
Window glass 2 mm.	3200 Å
Celluloid film	3000 Å
Crookes glass (Fused glass 83% and cerium nitrate 17%)	3650 Å
Crookes glass (soda glass 96·8%, Fe_3O_4 2·85% carbon and tartrate 0·35%)	96% infra-red absorbed
Crookes glass (containing rare earth oxides)	Nearly all visible transmitted, 3650 Å
Quartz with silver film	Transparent to ultra-violet only
Chance's ultra-violet glass	Almost opaque to visible, transmits 3900 to 3300 Å

For the purposes of quantitative work, it is necessary to have a light source which is, approximately, monochromatic. Some sources of light are themselves roughly monochromatic e.g. the light from a Bunsen burner into which a sodium salt is fed.

The requirements for a satisfactory light to be used as the source of monochromatic radiation are as follows: — (1) It must have high intensity. (2) It must be steady for relatively long periods. (3) Its spectrum should have a few very strong lines rather than a closely packed number of lines of moderate intensity. Quartz mercury vapour lamp satisfies most of these conditions, and that is why it is largely used in photochemical researches. On the other hand, when a less rigorous degree of monochromatism is required, "pointolite" and gas-filled tungsten filament lamps present certain advantages, and are extensively used by photochemists. When suitable light filters are used with these lamps it is possible to isolate strips of spectrum about 100 Å wide for quantitative work.

Light filters may consist of (1) dyed gelatine films, (2) coloured glasses, (3) solutions and (4) gases. Satisfactory coloured gelatin filters are prepared by Messrs. Kodak, Central Scientific Company, Chicago, and other manufacturers (Wratten light filters, Wallace M and S filters etc.). The physical characteristics and the transmission curves are specified by the manufacturers. Wratten gelatine filters are very satisfactory for many purposes because of the accurate standardization of several of these filters. The substance to be used as a light filter must be definite, reproducible, and fast to light even if warmed up. If colloidal, its absorption coefficient must also be unaffected by dilution, by lapse of time, or by any substance added. For the absorption of heat rays, Keyes (*U. S. Patent 1,237,652 (1917)*) uses a vacuum cell as a

protection against the heat of the lamp. A quartz water cell 1 cm. thick transmits 58% of 9450 Å and 14% of 11,900 Å radiations. For the absorption of infra-red rays, a 2% solution of cupric chloride, or corning glass filter G 392, 6—10 mm., and for the absorption of fluorescence radiation, solutions of fluorescein or rhodamine B or corning glass filter G. 371 R 2—3 mm. have been used.

Corning glass filters (*Bureau of Standards Technologic papers* 119 (1919); 148 (1920)) are very satisfactory when their thickness and consequent bulk are not objectionable, and transmit 3660 Å. These glass filters have transmission characteristics, and can be used in combination to obtain necessary effects.

Uviol glass permits ultra-violet up to 2530 Å to pass. According to Michaud and Tristan (*Scientific American* 107, 257 (1912)), quartz lenses coated with silver, obtained by the reduction of an alkaline silver salt solution with a 10% milk sugar solution, cut off practically the whole of the visible spectrum, and transmit ultra-violet rays (3160 to 3260 Å). Silver, either in the form of plates, or in the colloidal state, shows absorption up to 4000 Å, and on increasing the concentration of the colloid absorption in the short ultra-violet is noted.

Miethe and Stengel (*Z. wiss. Phot.* 18, 19, 57 (1919)) consider a list of various dyes suitable for ultra-violet ray filters, with the range of wavelengths which will be affected by different concentrations of the dye. According to Potapenko (*ibid.* 18, 238 (1918)), the most suitable form of light filter for uviol glass lamps is a stained gelatine film, and he gives complete directions for making dyed gelatine filters. Commercial filters available in the market include Agfa, Corning, Cramer, Fuess, Ilford, Jena, "Lifa", Maison Calmels, Wratten, and Wallace. Gibson and others (*Bureau of Standards Tech. paper* 148 (1920); *Scientific paper* 440 (1922)) have determined the transmission of certain glass filters and dyes. Hood (*Science* 64, 281 (1926)) describes glasses with considerable power of transmission.

Wood (*Phil. Mag.* vi, 5, 257 (1903)) observed that nitrosodimethylaniline absorbs rays of wavelengths 3900—5000 Å but transmits those between 2000 to 3900 Å. Thus nitrosodimethylaniline is an excellent filter, either in the form of stained gelatine films, or in solution, for obtaining ultra-violet light. Another light filter for ultra-violet rays in which cinchonine sulphate, triphenyl methane, etc. have been used, is described by Mannich (*Chem. Zeit.* 33, 1167 (1909)). The separation of visible from ultra-violet rays may be effected by a solution of quinine sulphate, which is almost colourless, and permits visible rays to pass through readily, while it is opaque to ultra-violet rays shorter than

4000 Å. Clark (*U. S. Patent* 1293039, Feb. 4 (1919)) has worked out a light filter for absorbing blue violet and ultra-violet rays by using gelatine or other light transmitting material, containing a salt of glucose phenylosazone pp'-dicarboxylic acid. Lehmann (*Chem. Zeit.* **33**, 1167 (1909); *Physik. Zeit.* **11**, 1039 (1910)) has recommended a vessel of Jena blue uviol glass, filled with copper sulphate solution, and coated on the outside with gelatine containing nitrosodimethylaniline, for the transmission of ultra-violet rays. He states that when a filter is prepared for cutting off a certain wavelength, it is advisable to add some other substance for removing the heat rays. Recently Eder (*Z. wiss. Phot.* **26**, 373 (1929)) has reported that the Davis -Gibson light filter with copper-cobalt solutions is a suitable one.

A saturated solution of cupric nitrate mixed with chromic acid eliminates the red and blue violet radiations. By a suitable change of the proportions, a greater or less degree of absorption at either end of the visible spectrum is attained. A solution of 1 gm. crystalline copper sulphate, 75 c.c. ammonium hydroxide (density 0.88) and 225 c.c. water transmits blue light of wavelengths 4050—4360 Å. Solutions of methyl violet and potassium dichromate transmit radiations 7180 to 6390 Å, solutions of cupric chloride and potassium chromate transmit 5400-5050 Å, copper sulphate and methyl green 5260—4580 Å, copper sulphate and methyl-violet 4780—4100 Å, and solutions of nickel sulphate, potassium chromate, and potassium permanganate transmit radiations 6140 to 5760 Å. According to L. Hill (*Proc. Roy. Soc. B* **102**, 119 (1927)) a saturated solution of uric acid (1 in 40,000), in a stratum 6 cm. thick, absorbs all rays of wavelengths shorter than 3200 Å, cutting out from the spectrum of the mercury vapour lamp the intense band at 3132 Å.

The following solution transmits the green mercury line 5460 Å: — 0.4 gm. picric acid, 3.5 grms. copper sulphate crystals, 15 grms. didymium nitrate in 300 c.c. water. Picric acid solutions show strong absorption in the region 4700—3500 Å. A very convenient filter for the transmission of wavelengths 5750—5800 Å consists of 15 grms. potassium bichromate, 3.5 grms. copper sulphate crystals, and 1 c.c. concentrated sulphuric acid in 300 c.c. water. According to Wood (*Smithsonian Institute* 155, (1911)), only infra-red radiations (greater than 6900 Å) are transmitted by a cell of dense blue cobalt glass filled with a saturated solution of potassium dichromate one centimetre or more in thickness. A saturated solution of iodine in carbon-disulphide is opaque to all visible radiations, and transmits freely the infra-red. Filters of normal potassium nitrite, and of N/20 copper sulphate 1 cm. thick, can cut off ultra-violet and heat rays.

Landolt (*Das optische Drehungsvermögen*, 2. Aufl. S. 387) recommends the following filters:

Red	$\left\{ \begin{array}{l} \text{Crystal violet 5 B. O. — 0.005 grm. in 100 c.c.} \\ \text{Potassium chromate — 10 grs. in 100 c.c.} \end{array} \right.$	$\left\{ \begin{array}{l} \text{transmits in 2 cms.} \\ \text{thickness 6659 Å} \end{array} \right.$
Yellow.	Potassium chromate — 6 grs. in 100 c.c.	$\left\{ \begin{array}{l} \text{transmits in 7 cms.} \\ \text{thickness 5890 Å} \end{array} \right.$
Light blue	$\left\{ \begin{array}{l} \text{Double green S. F. — 0.02 grm. in 100 c.c.} \\ \text{CuSO}_4 \cdot 5\text{H}_2\text{O — 15 grs. in 100 c.c.} \end{array} \right.$	$\left\{ \begin{array}{l} \text{transmits in 2 cms. thick-} \\ \text{ness 4885 Å} \end{array} \right.$
Violet	$\left\{ \begin{array}{l} \text{Crystal violet 5 B. O. — 0.005 grm. in 100 c.c.} \\ \text{CuSO}_4 \cdot 5\text{H}_2\text{O — 15 grs. in 100 c.c.} \end{array} \right.$	$\left\{ \begin{array}{l} \text{transmits in 2 cms.} \\ \text{thickness 4482 Å} \end{array} \right.$

According to Winther (*Z. phys. Chem.* **41**, 169 (1902)), the following are very convenient solution light filters:

Green	$\left\{ \begin{array}{l} \text{Violet yellow — 0.25 grm. in 100 c.c.} \\ \text{Cupric chloride — 60 grs. in 100 c.c.} \end{array} \right.$	$\left\{ \begin{array}{l} \text{transmits in 2 cms.} \\ \text{thickness 5332 Å} \end{array} \right.$
Dark blue	$\left\{ \begin{array}{l} \text{Crystal violet — 0.0025 grm. in 100 c.c.} \\ \text{Cupric chloride — 25 grs. in 100 c.c.} \end{array} \right.$	$\left\{ \begin{array}{l} \text{transmits in 2 cms.} \\ \text{thickness 4655 Å} \end{array} \right.$

For the transmission of blue light of wavelength 4360 Å, Vanino (*Preparative Chemistry I*, p. 500 (1921)) recommends: 3 cms. layer of 1% solution of aqueous tetrammino copper sulphate, combined with $\frac{1}{2}$ cm. layer of 6% aqueous quinine hydrochloride solution.

For the transmission of violet 4050 Å, 3 cms. layer of 0.02 N iodine in carbon tetrachloride solution, combined with $\frac{1}{2}$ cm. layer of 0.1% aqueous quinine hydrochloride solution is used. For 4360 Å, 0.5 cm. of 4% quinine bisulphate and 0.5 cm. of 0.085 victoria blue (Cassella) are recommended.

According to Wood (*Physical Optics* 1914, page 15), the following solutions will be found suitable:

Potassium bichromate transmits the green and the two yellow lines. Addition of neodymium salt to potassium bichromate removes the yellow lines. Blue cobalt glass and aesculin solutions transmit the line 4359 Å. Guinea green B extra (Berlin) and quinine sulphate transmit 4916 Å. Chrysoidine and eosin transmit the yellow line 5790 Å. The chrysoidine should be dilute and the eosin added until the green line disappears. A very thick cell with a saturated solution of potassium dichromate is perhaps as good. Methyl violet 4 R and nitrosodimethyl aniline transmit the ultra-violet line 3660 Å and feebly 3984 Å. For the transmission of 4359 Å Weigert-Kummerer (*Ber.* **46**, 1210 (1913)) recommends thick cobalt glass and 3% quinine sulphate solution of thickness 1 cm., and Winther (*Z. wiss. Phot.* **24**,

90 (1926)) suggests the following mixture: 0.0075 gr. rhodamine B (Höchst), 2 grs. quinine sulphate, 6 c.c. normal sulphuric acid in 100 c.c. water. Plotnikoff (*Photochem. Versuchstechnik*, Leipzig p. 20 (1912)), Luther and Forbes (*J. Amer. Chem. Soc.* **31**, 770 (1909)), Eggert and Noddack (*Zeit. f. Physik.* **20**, 301 (1923)), and others used 0.03 grm. diamond fuchsin 1 and 4 grms. quinine hydrochloride in 100 c.c. 96% alcohol, or very dark cobalt glass and 0.05% quinine sulphate for the transmission of the violet line 4050 Å.

For the ultra-violet line 3650 Å, Winther (*Z. Elektrochemie.* **19**, 389 (1913)) recommends 0.03 gr. neutral diamond fuchsin in 100 c.c. water (thickness 1 cm.). Weigert-Kummerer (loc. cit.) suggests 0.0007% nitrosodimethylaniline in water and copper sulphate solution for the absorption of infra-red radiations (compare Gray, *J. Physical Chem.* **31**, 1732 (1927)).

For ultra-violet 3130 Å, 0.001 normal aqueous solution of potassium chromate in quartz or uvioil glass cells of 1 cm. thickness seems suitable, because the mercury line 3660 Å is highly absorbed by this medium.

Saunders (*J. Opt. Soc. Amer.* **16**, 362 (1928)) has reported that one mm. of a solution of potassium hydrogen phthalate, containing 40.836 grms. per litre, transmits uniformly up to 3000 Å, and cuts off sharply at that wavelength. The salt should be purified by recrystallisation.

Dahm (*ibid.* **15**, 266 (1927)) has discussed the use of several organic media as spectral filters for ultra-violet light.

Terroux (*Trans. Roy. Soc. Canada* (3) **21**, iii, 255 (1927)), has stated that a 1% solution of rhodamine B, one cm. thick, transmits a narrow band from 6500 to 6100 Å. A 0.05% solution transmits freely over a broad band from 7000 to 5300 Å, and less freely between 4500 and 3700 Å. Outside these limits the solutions appear to absorb completely.

Gelatine and liquid filters must be kept as nearly as possible at room temperature.

The most useful of gaseous filters contain bromine and chlorine, or chlorine in quartz, and transmit 2540 Å. Chlorine shows a maximum absorption in the region 3800—3000 Å. Bromine vapour cuts off the visible part of the spectrum entirely up to 3800 Å, and its absorption capacity ends slightly beyond the point when the absorption of chlorine begins. In aqueous solutions the absorption of these two gases changes probably due to the formation of hydrates. According to Peskoff (*J. Phys. Chem.* **21**, 382 (1917)) two quartz vessels of 8 cms. thickness,

one containing chlorine and another bromine vapour, will allow only radiations of wavelengths 2300—2800 Å to pass through.

While nitrogen is transparent even at 1250 Å, oxygen absorbs from 1860 Å, a fact which prevents the shorter wavelengths from inducing photochemical reactions, except at very short distances from the light source. If the ozone formed by mercury vapour lamps is not removed by a current of air, radiations of wavelengths 2300 to 2800 Å will be absorbed to some extent.

The following summary of the ordinary light filters will be found useful (compare Ellis and Wells, *Chemical Action of Ultra-violet Rays*, page 80).

Liquid filters	Wratten filters	Corning glass	Radiation transmitted in Å
Methyl violet and nitrosodimethyl aniline	18 ultra-violet	G 586 A W 8—10 mm.	3650 3656 3663
Methyl violet and quinine sulphate or diamond fuchsin and quinine hydrochloride	36 Hg. violet	G 586 A 3—5 mm. and Novoiolo 0.4 mm.	4047 4078
Cobalt glass and aesculin or 3% quinine sulphate	50 Hg. blue.	Noviol A, 3.0 mm. and G 585 3—5 mm.	4359
Potassium dichromate and neodymium ammonium nitrate	62 Hg. green or 77 Hg. special or 77 A Hg. special for interferometry	G 555 Q 8—10 mm. and G 34 V 3.4 mm.	5461
Chrysoidine and eosin or saturated $K_2Cr_2O_7$ and $CuSO_4 \cdot 5H_2O$ and H_2SO_4	22 Hg. yellow	G 34 R 3—4 mm.	5769—90
Cobalt blue glass and saturated $K_2Cr_2O_7$	88 or 89 A	G 554 E K 6—8 mm.	infra-red ⁽¹⁾ (8500)

EXPERIMENTAL METHODS.

In quantitative experiments, it is ordinarily necessary to work under conditions enabling us to measure easily the amount of light absorbed. Hence vessels with parallel cylindrical rather than have to be used. The intensity of the incident light should be constant. In

(¹) Compare: Bhattacharya and Dhar (*J. Indian Chem. Soc.* (1930)).

tropical countries, sunlight can be used for quantitative work for a limited period. Other sources of light commonly used are: Tungsten filament lamp, Pointolite lamp, quartz mercury vapour lamp and uviol glass mercury vapour lamp.

The tungsten filament lamp and the Pointolite lamp give a continuous spectrum relatively poor in ultra-violet radiations. On the other hand, the mercury lamp gives out rays rich in shorter wavelengths, and the principal radiations in the mercury arc are:

Visible spectrum 6152, 5760, 5700, 5461, 4946, 4359, 4078, 4047 Å.

Ultra-violet 3650, 3131, 3126, 2967, 2652, 2537 Å.

The quartz mercury lamp allows radiations of wavelengths up to 1850 Å to pass through, and, if radiations of high frequency are used for the experiments, quartz cells have to be employed. Ordinary glass is transparent up to 3000 Å and uviol glass up to 2500 Å.

The light intensity of a lamp fed by electric current rapidly increases with the voltage. For a carbon filament lamp, the illuminating power is nearly proportional to the 6th power of the voltage. It is therefore necessary to maintain the voltage very constant in order to secure a constant light intensity. In order to obtain monochromatic light different methods have been utilized. The white light from a certain source, decomposed by a prism, and a narrow spectral region isolated is not intense enough, because the amount of light which enters the slit of a spectroscope is very small. For photochemical experiments lights filters which allow a spectral band to pass are used. The filters may be thin layers of coloured glass, or colouring matters in solution, or gelatine layers fixed on the glass surface. The filters are used with a light source giving a continuous spectrum. This method does not yield really monochromatic light, but radiations of wavelengths between two narrow limits are obtained.

The simplest method of varying the intensity of light in a known ratio is to change the distance of the lamp. Thin silk paper of known absorptive power has also been interposed between the light source and the reaction vessel to vary the light intensity. Rotating discs, with sectors of different sizes and numbers, have also been utilized; but this method yields light of which the intensity is not continuous, but varies intermittently and can only be used in special cases.

The temperature can be maintained constant by means of a thermostat, of which at least one side is transparent. In order to follow the course of photochemical reactions, as in the case of thermal reactions, different analytical methods have been used: — titration, measurement of the variation of the electric conductivity, absorption of light of a

given wavelength (spectrophotometric method), the measurement of the gas pressure, evaporation of the solution and determination of the melting point of the residue, etc. In several reactions, the finding out of a suitable method of analysis is a difficult question.

The experiments in the case of each of the reactions studied by Dhar and co-workers have been divided into four parts: — (1) the kinetics of the reaction at various temperatures both in the dark and in the light of different wavelengths have been determined. (2) The measurements of the energetics of the reactions in the same region of wavelength and temperature were carried out. (3) The light absorption by the reacting system in the visible portion of the spectrum has been observed by a Nutting's spectrophotometer, and (4) the change of the influence of the variation of intensity on the same reaction has been studied using different qualities of light.

The experimental arrangement adopted for these investigations was as follows:

A thermostat was maintained at a constant temperature, and water from it was circulated by means of an automatic syphon inside a hollow rectangular copper jacket having two opposite faces open. Within this copper jacket a closely fitting quartz cell with plane faces was kept, and a thermometer with graduations to one-tenth of a degree was always kept suspended in the quartz cell, through a hole in the quartz rectangular plate, which covered the cell in which the reaction took place.

The temperature could be controlled within $\pm 0.1^\circ$. The components of the reacting mixture were kept in the thermostat before mixing, in order to acquire the necessary temperature. A quartz lens was placed before the reaction vessel. A heliostat was set up, and sunlight was thrown upon the lens through an aperture in the room. The light was then made to pass through N/20 copper sulphate solution placed in a quartz cell to cut off most of the heat rays.

In order to carry out experiments in different ranges of wavelengths, the source of light used was a 1000 watt gas-filled tungsten filament lamp operated at 4.6 amperes. In some cases a Pointolite lamp was also used. The strength of current and voltage were maintained constant by means of a regulating resistance. Owing to the intense heating effect, an electric radiator was constantly used at the back of the lamp, which was kept in a wooden box lined inside with asbestos, and having a few holes drilled at the top. The hot air escaped through these holes.

Two big condenser glass lenses, one a double convex lens of focal length 13 cms., and the other a plano-convex lens of focal 18 cms. were

placed between the light source and the reaction vessel, in order to get maximum intensity and a parallel beam of light. To isolate different regions of wavelengths from the entire spectrum of light source, different solution filters (saturated dichromate solution kept in a cell made of cobalt glass and having a thickness of 1 cm., and other solutions) and a set of gelatin film "Wallace M and S" filters, or Wratten filters were used. The light filters were utilised in combinations of two at a time, in order to secure close range of wavelength. The filters were clamped just in front of the reaction vessel. Other arrangements were the same as in the experiments in sunlight.

The changes in the reactions studied were determined at noted intervals of time, by withdrawing some of the reacting mixtures and subjecting them either to suitable titrations or spectrophotometric measurements.

To determine the quantum efficiency (the number of molecules decomposed per absorbed quantum), the measurement of the absorption of energy by the reactants was necessary. To measure this a Boys's radiomicrometer with lamp and scale was used. The radiomicrometer was kept at a constant distance from the light source. The instrument was calibrated for the amount of energy absorbed to produce 1 mm. deflection on the scale behind it.

For the measurements of the light absorption by the reacting system, a Nutting spectrophotometer was used, and extinction coefficients in the different parts of the visible spectrum were determined.

To study the effect of variation of intensity, the experimental arrangements were the same as have already been described, with the modification that an Iris diaphragm was placed before the light filters clamped just in front of the reaction vessel. It was so arranged that no light other than that passing through the aperture of the diaphragm could fall on the reaction vessel.

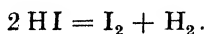
In all the experiments the thermal effects were deducted from the total changes obtained in light, in order to get the change due to light alone. The intensity of the light was taken to be proportional to the area of the aperture through which the light passed before falling on the reaction vessel.

CHAPTER IV.

General Considerations on the Kinetics and Mechanism of Photochemical Reactions.

The first fact to be noticed is the diversity of the formulae which express the velocity of the photochemical reactions in terms of the concentration and the light intensity. If it is assumed that the velocity is simply proportional to the quantity of light absorbed, it can be said without exaggeration that the velocity expression for each reaction presents an individual character, and depends on the mechanism of the chemical reaction. It is essentially variable according to the reaction under consideration, and consequently it seems useless to search for a general relation applicable to all cases.

The influence of concentration on the velocity of a reaction is not usually the same in the photochemical reaction as in the thermal one, but in several reactions Dhar and Bhattacharya have shown that the order of the photochemical reaction is the same as the thermal one. It should however, be remarked that a difference in the velocity expression does not always imply a difference in the mechanism of the reaction. The thermal decomposition of hydriodic acid is bi-molecular. Hence it has to be assumed that two molecules decompose simultaneously according to the following equation:



On the other hand, the photochemical decomposition of hydriodic acid is simply proportional to the quantity of light absorbed and consequently the order of the reaction is unity when the absorption is weak and zero when absorption is complete. This, however, does not exclude the possibility of the reaction taking place between two molecules, and Stern and Volmer have assumed that each active molecule of HI reacts with an inactive molecule in order that the quantum yield may have the value two. It appears, therefore, that the mechanism of the thermal and the photochemical reaction is the same although the formulae of the velocities are different.

A photochemical transformation has generally no definite order, as in the case of a thermal reaction. The notion of the order of a reaction implies that the expression of the velocity should have the following form:

$$v = K C_1^{n_1} C_2^{n_2},$$

where n_1 and n_2 are constants. This notion is not applicable to a photochemical reaction when the absorption is neither feeble nor complete; in such a case the velocity is an exponential function of the concentration of the photosensitive substance. One can naturally express the velocity in such a case for a short interval of time by an equality such as the foregoing one; but the exponent n corresponding to the photosensitive substance is no longer a constant, but increases as the concentration decreases. When one passes from feeble absorption to total absorption the order changes ordinarily by unity. However, this rule is not without exceptions. It is verified necessarily when the Grotthus-Draper law is applicable, but it fails when the law is not applicable.

PRIMARY DISSOCIATION OF PHOTSENSITIVE SUBSTANCES.

In certain cases the molecules excited to the Bohr state by absorption of light are themselves simply transformed, or react with molecules of the acceptor. In some cases these excited molecules undergo a dissociation into free atoms, which represent a second active condition, and react with a substance which is not photosensitive. This dissociation has been brought in evidence for several reactions involving bromine or iodine, and the velocities of these reactions are proportional to the square root of incident radiation. Also in several cases dissociation of the molecules into atoms on illumination is assumed to take place even when the reaction follows the Grotthus-Draper law; it would seem rather extraordinary that the molecules of bromine or iodine should dissociate by the action of light in aqueous solutions containing potassium oxalate, or in carbon tetrachloride solution containing cinnamic acid, but not in presence of other acceptors. The hypothesis of the dissociation into atoms seems to throw light on the mechanism of such reactions as the action of Cl_2 on CCl_3Br , oxidation of CCl_3Br by oxygen in presence of Br_2 , decomposition of ozone in presence of chlorine etc., which follow Einstein's law of equivalence even when the concentration of the acceptor is very small. It has been assumed that in such cases the concentration of the halogen in the atomic state is very small, and

consequently in presence of an acceptor even, in very small quantity, a free atom has more chance of meeting a molecule of the acceptor with which it can react than another atom with which it can combine, and thus there is a possibility that the Einstein law of equivalence is applicable in these cases.

The law of Grotthus-Draper is more general than the law of equivalence, but it is not sufficient by itself for the determination of the kinetics of a photochemical change. The quantity of matter transformed is sometimes simply proportional to the quantity of light absorbed, but often it depends also on the concentrations of the reacting substances over and above their influence on absorption. It also happens that the velocity may not be directly proportional to the light intensity, as demanded by the law of absorption of Grotthus-Draper. The variations of photochemical effect, as a function of light intensity and concentrations of the reacting substances, are of great interest, because these studies lead to important conclusions regarding the mechanism of the photochemical reactions. The determination of the quantum yield is equally important.

Moreover, the progress of a photochemical reaction is often profoundly modified by the presence of catalysts. Sometimes their intervention is necessary for the occurrence of the reaction, but very often their action is less important, and the photochemical change takes place also in the complete absence of all catalytic action.

In the investigation of the influence of the light intensity and concentrations on the velocity of a photochemical reaction, we have to consider two cases. In the first group the photochemical effect is simply proportional to the quantity of light absorbed, and in the second group the velocity depends not only on the amount of light absorbed but also on the concentrations of the substances which undergo chemical changes, independently of the variations of absorption.

CLASSIFICATION OF PHOTOCHEMICAL PHENOMENA.

In order that a photochemical reaction may take place when a system is exposed to light, it is necessary that the system should contain a simple or compound substance possessing capacity for chemical reaction, and be capable of absorbing radiations of short wavelengths. It should be stated that substances of diverse composition are photo-sensitive, and the photochemical reactions themselves belong to highly different types.

Light causes or accelerates decomposition, phenomena of oxidation or reduction, substitution, addition, polymerisation, intramolecular transformation, allotropic modification, and synthesis (photosynthesis).

A systematic classification of photochemical reactions is very difficult, because often one and the same reaction passes from one class to another according to the experimental conditions, whatever may be the basis of classification. Hence we shall only mention some characteristics of the principal groups of photochemical phenomena.

Already in 1847, Helmholtz recognised that photochemical reactions can be divided into two main groups: — (1) In the first group, light only accelerates a transformation which takes place spontaneously in the dark, and hence there is diminution of free energy in such systems. (2) The second group of reactions cannot proceed by themselves, and light supplies the necessary energy. Different designations have been proposed for these two groups of phenomena. Warburg (*Verh. d. deutsch. phys. Ges.* 757 (1907)) distinguishes them as *reactions of the first kind* and *reactions of second kind*, whilst Weigert (*Die chemischen Wirkungen d. Lichts*, 193 (1911)) uses the expression "reactions productive of work" and "reactions which accumulate work". The reactions of the first kind have also been called catalytic reactions by some authors, who include the action of light in the phenomenon of catalysis, but this view is not free from criticism. For the sake of simplicity the reactions in the first group may be called *exoenergetic reactions*, i.e. reactions capable of giving out energy, and the reactions in the second group, which are associated with an increment of free energy, are designated as *endoenergetic reactions*.

Few endoenergetic reactions were known previously, because most of these reactions take place in ultra-violet light. Amongst the endothermic reactions which take place in visible light, can be mentioned the carbon assimilation by plants, and the decomposition of silver chloride and silver bromide. The following endoenergetic reactions have been studied in ultra-violet light: the formation of dianthracene from anthracene, ozone from oxygen, photochemical decompositions of HCl, HBr, H₂O, NH₃, CO₂ etc.

The exoenergetic reactions are very numerous, and include those ordinarily investigated in visible radiations.

From another point of view, one can divide photochemical reactions into *irreversible* ones, which can continue till one or more of the re-

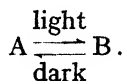
acting substances disappear completely, and *reversible* ones, which lead to a photochemical equilibrium. The distinction between these two groups is not absolute. It is probable that in certain reactions, which are considered as irreversible, the transformation is not absolutely complete, but the amount of matter unchanged is too small to be measured. On the other hand, change of the experimental conditions suffices to make an irreversible reaction into a reversible one. Thus the photosynthesis of hydrochloric acid is irreversible in blue light, but becomes reversible in ultra-violet. The irreversible reactions are for the most part exonergetic; many of these reactions take place in the dark slowly, and hence it is necessary to distinguish between purely photochemical reactions of which the velocity in the dark is zero or negligible (synthesis of HCl), and mixed photochemical reactions, in which the photochemical reaction is superposed on that which spontaneously takes place in the dark.

The presence of small quantities of a foreign substance, which does not modify the absorption, can occasionally retard or accelerate a photochemical reaction. This is photochemical catalysis. Most of the photochemical reactions, which may be called direct photochemical reactions, are produced by the light absorbed by one or both of the reacting substances; but there are reactions, which can be rendered tensitive by the addition of a suitable substance which is not destroyed in the course of the reaction, and these are called photosensitised reactions.

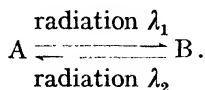
Gerke (*J. Amer. Soc.* **49**, 2671 (1927)) has divided photochemical reactions into three classes according as the absorption of light produces excited atoms or molecules, causes a decomposition of molecules into atoms, or excites a catalyst or sensitiser. A given photochemical reaction may belong to the first class in one region of the spectrum and to the second class in another region. Reactions of the second class, but not of the first class, have quantum yields independent of the pressure and wavelength of the light.

Photochemical reactions can be roughly divided into 3 groups:

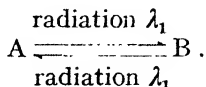
(1) One of the two reversible reactions is photochemical, whilst the opposite reaction is spontaneously produced in the dark, and is not influenced by light. The phenomenon can be represented by the following scheme:



(2) Both the opposing reactions are photochemical in nature, but are sensitive to radiations of different wavelengths:



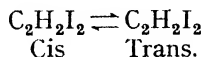
(3) Both the reactions are photochemical in nature and are sensitive to the same radiations:



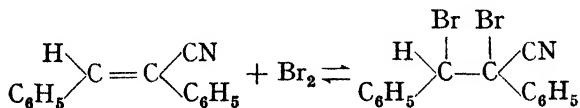
In all these cases the system when exposed to light tends to assume the stationary state, which is ordinarily called photochemical equilibrium. This equilibrium is reached when the antagonistic reactions have equal velocities. There is no hard and fast rule between reversible and irreversible transformations. One and the same reaction can pass from one category to the other under different experimental conditions. Thus, for example, the photosyntheses of HCl and phosgene gas are irreversible at the ordinary temperature and under the action of visible light, but these reactions become reversible at high temperatures and under the ultraviolet radiations. There are several other cases of this type. The reactions of the third group are supposed to take place in the dark, and light only accelerates the velocities of the reactions without affecting the equilibrium. The following reactions are supposed to belong to this group: —

(a) The synthesis of phosgene gas in presence of light at a high temperature.

(b) Transformation of isomers of Cis-form to the Trans-form, e.g.:



It is assumed that in both these reactions, there is the probable formation of a catalyst, which accelerates both the antagonistic reactions. A similar conception has been advanced to explain photochemical sensitization. The reversible action of bromine on α -phenyl cinnamonnitrile represents a different case:



The law of mass action is not applicable to this photochemical equilibrium. According to Berthoud, a bromine atom, which is the active agent, does not accelerate the two antagonistic reactions in the same ratio, and hence a bromine atom cannot be included in the category of a catalyst.

As a general rule light displaces the equilibrium established in the dark, and a photochemical stationary state is profoundly different from an ordinary chemical equilibrium, although it results also from the equality of the velocity of the opposing reactions. In a photochemical stationary state the free energy is not at its minimum, and the photochemical stationary state is maintained only by the action of light. When, therefore, the radiation stops, a true equilibrium is established more or less quickly. Finally, a catalyst need not necessarily have the same action upon the two opposing reactions, and can thus produce a displacement of the stationary state. The principles of thermodynamics, which are directly applicable to true equilibria, are without help in the study of the photochemical stationary state. In the last case, the relation between the concentrations of the different reacting substances in the system is not expressed by the law of mass action, and cannot be predicted theoretically. The relation depends on the courses of the opposing reactions, and is empirically determined in each particular case. The number of reversible photochemical reactions is large, but few quantitative measurements are available.

ENDOENERGETIC AND EXOENERGETIC REACTIONS.

The fact that in exoenergetic phenomena, light simply accelerates a transformation which takes place spontaneously in the dark, has led certain authors to include the action of light as a part of catalysis. It seems probable that in the photochemical transformations in which the quantum yield is very high, light creates a catalyst. This is, however, not a characteristic of exoenergetic reactions. There are several exoenergetic reactions which follow the Einstein law of equivalence, or where the quantum yield is less than the theoretical value; and in these the generation of a catalyst seems unlikely.

On the other hand, the action of light cannot be included exactly in the category of catalysis. When light acts on a chemical system, it always supplies energy to the system, and it frequently accelerates a reaction, but not the reverse reaction, and hence the equilibrium established in the dark is modified. On the other hand, a catalyst is not a source of energy; it always accelerates the two opposing reactions in

the same ratio, and does not displace the equilibrium. Light acts in the same manner on endoenergetic and exoenergetic reactions. The experiments of Warburg (*Sitzungsb. d. preuss. Akad. Wiss.* 746 (1911)) on the decomposition of ammonia are interesting from this point of view. Warburg studied this reaction under the conditions where the gaseous mixture tends to an equilibrium in the dark $2 \text{NH}_3 \rightleftharpoons \text{N}_2 + 3 \text{H}_2$. The equilibrium is attained when 1.2 % of the ammonia is decomposed. He allowed ultra-violet light to fall on pure ammonia and on a mixture containing 50 % NH_3 and 50 % of a mixture of nitrogen and hydrogen ($\text{N}_2 + 3 \text{H}_2$). In both the cases, the ammonia was decomposed. In the first case, the system under the action of light approached the state of equilibrium, whilst in the second the equilibrium was not reached and the system was further from the equilibrium condition. The reaction is thus exoenergetic in the first case and endoenergetic in the second. The yield remains the same when the same amount of absorbed light energy is considered.

In all photochemical phenomena, light has always the primary effect of activating the molecules, which subsequently either decompose or react with other molecules. If the reaction is exothermic, the quantity of heat given out in the second phase of the transformation is greater than the energy of activation. The reverse would be the case with endoenergetic reactions. The exoenergetic reactions are distinguished from the endoenergetic ones by the values of quantum yield. In the former group of reactions, the quantum yield can have any value; whilst in the second, because the light supplies the energy necessary for the carrying out of the reaction, the yield is necessarily limited, and it is difficult to predict the maximum yield by calculations based on thermodynamics. It should be remarked in particular that the quantum yield cannot be calculated from the heat absorbed in the reaction. For example, with radiations of wavelength 6100 Å, the product $Nh\nu = 45,000$ gram calories. One may assume that this quantity of light can at most transform a quantity of matter in which the heat absorbed is equal to 45,000 gram calories. In reality, the photochemical effect thus calculated does not represent a limit which would not be surpassed. It can be conceived that the action of light would be followed by endothermic reactions, and thus a photochemical reaction can produce a cooling effect notwithstanding the fact that the system is receiving radiant energy. This possibility has been discussed by Weigert for chlorophyll assimilation. What is essential for causing a reaction connected with an increment of the free energy is not the communication of heat to the system, but the supply of necessary energy either by

the action of light or by the electric current. Consequently, we should try to compare the energy spent in the reaction and the increase in the free energy due to the absorption of light, but actually this comparison is not possible. The work which has to be spent is only known for a few reactions. On the other hand, the radiant energy cannot be completely transformed into work. When this is not the case, the yield would be less than unity but it is impossible to foresee the value of yield in these photochemical phenomena.

CHAPTER V.

✓ The Law of Photochemical Equivalence.

A starting point for the rapid growth of photochemistry along new lines was undoubtedly the introduction of the quantum theory by Stark (*Physik. Z.* **9**, 898 (1908); also *Prinzipien der Atome-Dynamik*. II, 207 (1911)) and by Einstein (*Ann. Physik.* **37**, 832 (1912)). The attention of scientists turned from comparatively unsuccessful thermodynamic studies to a quantitative study of photochemical kinetics; and this resulted possibly in a clearer understanding of the function of radiant energy in producing chemical changes, and in throwing light on the mechanism of chemical reactions.

Stark, from considerations on atomic and molecular structure, was led to the assumption that, in certain cases, the rate of photochemical change is determined by the number of absorbed light quanta. His theory, clothed in qualitative language and not given the dignity of a thermo-dynamical deduction, did not receive from photochemists the attention it deserved. In Stark's papers, not only a clear distinction between the primary and secondary stages of a *direct* photochemical change, but an equally clear distinction between the mechanism of *direct* and *indirect* (including sensitised) reactions has been emphasised.

The application of the quantum theory to photochemistry dates in practice from the enunciation by Einstein in 1912 of the so called "**photochemical equivalent law**", which states that *in a photochemical reaction, one quantum of active light is absorbed per molecule of absorbing and reacting substance which disappears*. This simple and attractive relation, put forward with the authority of Einstein, has proved a great stimulus to research. This relation has proved itself a working hypothesis of great value.

In dealing with Einstein's work on this subject, we should distinguish between his thermodynamic proof of the law and his subsequent quite different deduction of the same relation. In the first case, an exact mathematical proof of what may happen under the ideal conditions is laid down, the other is practically a mere statement of what obviously will be the approximate result under another given set of conditions.

The thermodynamic proof appeared first in two German papers (*Ann. der Physik* (IV), **37**, 832; **38**, 881 (1912)) and then with a slightly different treatment, as a single French paper (*Jour. de Phys.* **3**, 277 (1913)).

"In this proof a reversible gaseous reaction of the type $xy + e \rightleftharpoons x + y$ is considered. The dissociation takes place as a necessary consequence of, and solely by the absorption per molecule of xy , of a mean quantity e of radiant energy of frequency ν ; and the recombination of x and y takes place according to the mass action law solely with the simultaneous liberation of a mean value of e units of radiant energy of frequency ν per molecule of xy formed. The reaction is thus a completely reversible one. If now ρ is the black body radiation density for frequency ν at temperature T , then we are simply dealing with an ordinary thermal equilibrium. As a general case, however, Einstein imagines an equilibrium in which the radiation density ρ corresponds, not to T , but to T_s , where T_s is higher than T . Such a pseudothermodynamic equilibrium (such an equilibrium is not of course to be confounded with the ordinary "stationary state" of the photochemist) is clearly only imaginable in a closed space, the walls of which are internally completely reflecting, and under such conditions is stable. Einstein considers a small virtual change from this pseudoequilibrium state, equates to zero the sum of the entropy changes in the gas, the radiation, and the constant temperature reservoir which surrounds the gaseous system, and arrives at a connection between ρ and T_s which, provided that the conditions are in other respects those under which Wien's radiation law is valid, leads directly to the identity

$$e = h\nu \text{ (the Einstein Law).}$$

"In the course of the proof, Einstein shows that e , under such conditions, *must be independent* of T . On the other hand, in the early part of the 1913 paper, he states that e may be dependent on T . "It should be emphasised that e is the mean energy absorption per molecule decomposed." Later, assuming, as happens in practice, that a whole range of frequencies is active in causing decomposition, and that the total decomposition is the sum of those caused by the single elementary frequencies, he shows that ν in the above formula, is the frequency of the radiation, and has nothing to do necessarily with any characteristic frequency within the molecule. Finally, it may be noted that although deduced for a particular type of truly unimolecular gas reaction, Einstein expressly states that the result is a general one, and can be ex-

tended to more complex gas reactions or to reactions taking place in dilute solution.

Einstein's *deduction* (*Verh. d. deut. Physikal. Ges.* **18**, 318, (1916)) of the photochemical equivalent relation follows quite different lines. The absorbing and reacting molecule is regarded as a kind of generalised Bohr Model, capable of existence only in a definite series of energy (Bohr) states, and passing from one state to another by absorption or emission of a quantum. He considers two such states Z_m and Z_n , of corresponding energy contents E_m and E_n , where $E_m > E_n$ and $E_m - E_n = h\nu$. After dealing with such a system in temperature equilibrium, he takes the special case where T is such that ρ the radiation density corresponding to frequency ν , is very low. Practically all the molecules will be in the Z_n (lower) quantum state. He further assumes that a molecule in the Z_m state, besides reverting to the Z_n state with emission of $h\nu$, can also and *far more rapidly*, undergo a different change analogous to a unimolecular reaction—say $Z_m \rightarrow W$. Clearly then, in such a system, insulated with radiation of frequency ν from a source at a temperature higher than T , one molecule in the Z_m state will be formed per absorbed quantum, and *almost all* will react further to give W , which corresponds to the practical validity of the law. It is of special importance here to note that the *primary and secondary* reactions are clearly distinguished, which was not previously the case, and that the primary product, for the formation of which the law implicitly holds, is a higher quantum state. The process considered is, therefore, in appearance at all events, very different from that discussed in the thermodynamic proof.

The quantity of radiant energy E necessary for the transformation of a gram molecule of the photosensitive substance is given by the relation:

$E = N h \nu$ ergs = $\frac{N h \nu}{4.186 \times 10^7}$ gram calories, where N = the Avogadro number. On substituting the values of N and h , we get

$$E = \frac{60.7 \times 10^{22} \times 6.55 \times 10^{-27}}{4.186 \cdot 10^7} \times \nu,$$

= $95 \times 10^{-12} \nu$ gram calories, or substituting the value ν by $\frac{c}{\lambda}$ and expressing λ in microns we get

$$E = N h \nu = 95 \times 10^{-12} \times \frac{3 \times 10^{10} \times 10000}{\lambda} = \frac{28,500}{\lambda} \text{ gram calories.}$$

The law of Grotthus-Draper expresses a proportionality between the photochemical effect and the quantity of absorbed light, but leaves the factor of proportionality undetermined. For determining the value of this factor, relative measurements of absorption are not sufficient; but absolute measurement of absorbed energy is necessary. Such measurements have now been carried out with a large number of photo-sensitive systems, and the ratio between the photochemical effect and the quantity of the radiant energy absorbed, expressed in calories or ergs, is known with numerous reactions.

Warburg, to whom we owe important research in this domain, has given the name "photochemical yield" to the fraction of energy absorbed which is transformed into chemical energy. It will be interesting to mention that this factor has great practical importance in such case as in the transformation of radiant energy into chemical energy, in the carbon assimilation in presence of chlorophyll.

Bodenstein, (*Z. physik. Chem.* **85**, 329 (1913)) stimulated by the theoretical considerations of Stark, calculated the quantum yield, or the number of reacting molecules per absorbed light quantum, of several reactions which had been studied previously by different photochemists. These calculations were only of an approximate character, since no direct measurements of the light energy absorbed in different photochemical reactions were available at that time. He deduced the different values by comparison of the geometrical arrangement in various experiments with the partially known absorption spectra of the reacting substances, and with the known energy distribution in the emission spectra of the light sources used.

Bodenstein concluded that some reactions nearly followed the law of equivalence, whilst in others (like the combination of chlorine and hydrogen, decomposition of ozone, acetone etc., bromination of toluene) the relation fails altogether. Although Bodenstein's view of the primary ionization of molecules on light absorption, as the explanation of the mechanism of photochemical reactions, had to be given up, the importance of his work lies in the acceptance of the equivalence law, and his attempt to explain the deviations.

Recently Taylor (*J. Phys. Chem.* **32**, 516 (1928)) has stated that the Grotthus-Draper law of absorption should be considered as the first law of photochemistry and the second as, "The absorption of light is a quantum process involving one quantum per absorbing molecule or atom. The photochemical yield is determined by the thermal reactions of the systems produced by the light absorption."

STERN AND VOLMER CONCEPTION OF THE PRIMARY PROCESS.

According to Stern and Volmer (*Z. wiss. Phot.* **19**, 275 (1920)) a molecule on absorption of light is not usually dissociated into atoms, but is raised to a higher quantum state, becomes activated and possesses a high reaction ability, and will undergo a chemical reaction on collision with some suitable inactive molecule present in the system. Moreover, it has been assumed that the re-emission of the light energy, and the loss of excitation energy by inelastic collisions with inert gas molecules, also take place, and both these factors account for the low quantum yield observed with certain reactions.¹ Since diatomic, and particularly, polyatomic molecules possess a large number of quantum levels, the loss of excitation energy will occur, in general, in several steps, and thus the absorbed light energy will be gradually dissipated and converted into heat energy.¹

Stern and Volmer suggested that the excited molecules lose their energy more readily on collisions with molecules of electronegative than with those of electropositive gases, and this suggestion is assumed to account for the retarding influence of oxygen on the velocity of certain photochemical reactions. These authors criticised the Warburg-Nernst view of primary dissociation of molecules into atoms on illumination, and pointed out in support of their conception that, in the case of iodine vapour, spectroscopic observations show that iodine molecules remain undissociated even on absorption of light quanta larger than their heat of dissociation. Luther, Stark, and others had vague ideas about the existence of activated molecules, and Bodenstein utilised the conception of activated molecules in the photochemical reaction between chlorine and hydrogen before the publication of Stern and Volmer's views. Later on, Christiansen and Kramers (*Z. physik. Chem.* **103**, 91 (1922); **104**, 451 (1923)) gave out the view that chain reactions caused by activated molecules are a general phenomenon, and are not restricted to photochemical processes, and that the products of a reaction of activated molecules must possess a large surplus of energy, equal to:

$$A = h\nu + q + \frac{1}{2}mv^2.$$

The first term of this equation is the absorbed radiation energy, which starts the reaction, the second is the heat of reaction, and the third is the kinetic energy of the reactants previous to the starting of the reaction. This excess of energy is transmitted by the products of reaction to other molecules of the reactant, and thus the activated

molecules are continuously regenerated. Christiansen and Kramers suggested that at least a part of the energy is present in the form of kinetic energy of translational motion, and activated molecules have therefore been designated as "hot" molecules.

FRANCK'S VIEWS ON THE PRIMARY PROCESS.

Recently Franck (*Trans. Farad. Soc.* **21**, 536 (1925)) has pointed out that according to the quantum theory of light absorption, the immediate result of such absorption by a molecule is the formation of an excited molecule, but that an excited molecule can undergo dissociation even without collisions with neighbouring molecules.

Absorption of light by homopolar molecules results always in an increase of the energy of their electronic system, coupled with a change of oscillatory energy of the atoms. Franck suggests that, in cases where the binding forces between the atoms are weakened by the increase of the electronic energy of the molecule, light absorption causes an increase of the oscillatory energy, and the molecule can undergo a dissociation as a primary process without the intervention of collisions, (this process is designated by Franck as adiabatic dissociation) provided the energy of absorbed radiation is large enough for this purpose. Of the resulting atoms, one will be in the normal quantum state, and the other will be excited, because of the fact that prior to dissociation, one of the electrons in the molecule was raised to a higher quantum state. If, on the other hand, the binding forces between the atoms are unchanged, or strengthened by the electronic excitation within the molecule, there is little chance of the molecules being adiabatically dissociated on light absorption.

The relation of the strength of the molecular binding to the excitation of the atoms can be approximately deduced from observations on the absorption spectra of molecules. Franck suggests that the halogen molecules belong to the type in which the absorption of radiant energy is accompanied by an adiabatic dissociation, whereas such unstable compounds as the mercury molecule Hg_2 , which is formed only on collisions of excited mercury atoms with normal atoms, belong to an entirely new group (third group). In the second group belong molecules of oxygen and nitrogen.

Moreover, Franck pointed out that in heteropolar molecules, light absorption leads to changes in oscillatory quantum energy, as is shown by their absorption spectra, independently of the change in the electronic system. Franck also comes to the conclusion that if an adiabatic

dissociation of heteropolar molecules takes place, then ions and not atoms will be formed, since the ions and not the atoms are the oscillating parts of the molecule.

Hogness and Franck (*Z. Physik.* **44**, 26 (1927)) have stated that if a molecule undergoes photochemical decomposition, associated with a work term D , due to the absorption of a quantum $h\nu$, then the excess energy $h\nu - D$, should appear as excess translational energy of the atoms or molecules of the decomposition. They have investigated the photochemical decomposition of sodium iodide vapour at 650° .

The most important fact now necessary for a complete understanding of the manner in which reactions are brought about by light energy is a knowledge of the action produced directly upon its absorption by the molecule.

WEIGERT'S VIEWS ON THE PRIMARY PROCESS.

Weigert (*Z. Elektrochem.* **14**, 591 (1908); **23**, 357 (1917); *Z. physik. Chem.* **102**, 416 (1922); **106**, 426 (1923)) has developed a theory of photochemical reactions in which a sharp distinction is drawn between ideal photochemical reactions and ordinary photochemical reactions. The equivalence law is valid only for the ideal processes, and the deviations in the cases of ordinary photochemical reactions are due not so much to the secondary reactions as to the fact that the whole Bohr concept of light absorption is strictly valid only for atoms and molecules in the highly diluted condition. In ordinary photochemical reactions we deal usually with concentrated systems, and here the mutual influences of the neighbouring molecules play an important rôle, and the deviations from Beer's law of absorption frequently observed are only an indication of this effect.

Moreover Weigert assumes that in gases and solutions certain clusters consisting of groups of molecules are formed on illumination, and that this process can change the normal absorption spectrum of a substance. The absorbed quantum is likely to be distributed amongst all components of the cluster, and the amount available for a chemical reaction becomes less. Weigert states that the size of the optical clusters, which determines the rate of a photochemical reaction, decreases with decreasing temperature, concentration, and wavelength of absorbed radiation. Weigert explains the primary process on light absorption as an inner photoelectric effect, and an intermediate formation of ions within the optical clusters. It is assumed that the energy required to ionize a gaseous molecule is greatly diminished by the presence of dipole mole-

cules in the clusters and other electronegative molecules behaving as electron receivers.

BALY'S VIEWS: — Baly (*Rec. trav. chim.* **41**, 514 (1922)) advanced a specific form of quantum theory, in which the free atoms are assumed to possess characteristic emission and absorption frequencies situated in the infra-red part of the spectrum. The frequencies are assumed not to change if the atoms combine to form molecules. The products of a photochemical reaction are supposed to emit radiation of those frequencies specific for the atoms forming the molecules, and the same frequencies are assumed to be reabsorbed by the reacting molecules, since they are composed of identical atoms. In this way, Baly tries to explain the formation of reaction chains caused by the excitation of a single molecule on absorption of light.

WARBURG'S RESEARCHES.

Previous to 1912, Warburg was occupied with the measurements of energy changes in photochemical reactions, and hence he was prepared to test the Einstein relation experimentally; and his researches are characterised by skill and accuracy, and clear interpretation of experimental results. We also owe to Warburg a nomenclature which derives naturally from the Einstein relation.

The fundamental photochemical equivalent (p) has been defined as the number of gram mols required for the absorption of one gram calorie of radiant energy of frequency ν , and consequently the number of gram moles primarily decomposing per absorbed gram calorie. We have $p = \frac{4.186 \times 10^7}{N h \nu} = \frac{\lambda}{28,470}$ mols, where λ is expressed in microns, h is 6.554×10^{-27} and $N = 6.062 \times 10^{23}$. Corresponding to p , the theoretical figure which is reached only when the Einstein law is implicitly obeyed, we have Φ , the *specific photochemical effect*, or the *effective photochemical equivalent*, which is purely an experimental magnitude expressing the final results of an actual photochemical reaction, and therefore includes the effects of all partial reactions, whether primary or secondary. The term *effective photochemical equivalent* expresses the number of absorbing gram molecules actually decomposed per absorbed calorie, whilst the term *specific photochemical effect* may refer either to moles of absorbing reactant (disappeared), or of resultant produced. Finally, the quantum efficiency γ represents the number of molecules which have reacted per absorbed quantum. It is given by the ratio $\frac{\Phi}{p}$ where Φ refers to the absorbing reactant, not to

the resultant, and is therefore the ratio of the *effective* to the *fundamental* photochemical equivalent, and becomes equal to unity if the law holds.

There is obviously an analogy between these magnitudes and those suggested by Faraday in connection with electrolytic decomposition. Thus to the Faraday which is 96,500 coulombs per gram equivalent, corresponds the equivalent radiant energy $\left(\frac{1}{p}\right)$, these which is $\frac{28,470}{\lambda}$ calories per absorbing gram molecule. And whilst in electrolysis we have fractional current efficiency = $96,500 \times \frac{\text{equivalents produced}}{\text{coulombs passed}}$, we have in photolysis, quantum efficiency

$$= \gamma = \frac{28,470}{\lambda} \times \frac{\text{mols decomposed}}{\text{calories absorbed}}.$$

In the following table the values of E and p , obtained with different wavelengths, are recorded:

8000 Å	7000 Å	6000 Å	5000 Å	4000 Å	3000 Å
E 35,600 Cal.	40,700 Cal.	46,500 Cal.	57,000 Cal.	71,200 Cal.	95,200 Cal.
p 0.0000281	0.0000246	0.0000210	0.0000175	0.0000140	0.0000105 gr. mols.

The results obtained by Warburg are in general not very favourable to strict application of the equivalence law. The following are the results of Warburg:

Decomposition of Hydrogen iodide. — This reaction was discovered by Lemoine in 1877, and later studied by Bodenstein (*Z. physik. Chem.* **22**, **23** (1897)) in sunlight, and found to be unimolecular. The absorption spectrum of HI and its decomposition under the action of ultra-violet light was later studied by Coehn and Stuckard (*ibid.* **91**, 722 (1916)). The absorption starts at about 3300 Å and increases for shorter wavelengths. The decomposition under the action of light of wavelengths longer than 2500 Å is complete and only light of shorter wavelength causes a partial formation of HI at about 270°, the temperature of their experiments. Warburg (*Sitzb. Preuss. Akad.* **300** (1918)) studied the reaction at room temperature, and used monochromatic light of three different wavelengths as the source of illumination. The following table represents the results of Warburg:

Wavelengths	2070 Å	2530 Å	2820 Å
$\frac{\text{Mols decomposed}}{\text{calories absorbed}} \times 10^5$			
Found	1.447	1.85	2.08
Calculated	0.73	0.89	0.993
Ratio	1.97	2.08	2.09

These results indicate that, on absorption of one quantum of light energy, two molecules of HI are decomposed, irrespective of the wavelength of the incident radiation. Recently, Bodenstein and Lieneweg (*Z. physik. Chem.* **119**, 123 (1926)) found that an increase in temperature from 150° to 175° kept the velocity of the reaction unchanged. In presence of iodine, the rate of reaction is retarded. Even liquid HI decomposes at the room temperature at the rate of two molecules per light quantum.

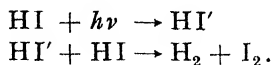
Warburg and Rump (*Z. Physik.* **47**, 305 (1928)) have used highly purified hydrogen iodide dissolved in hexane, and in water, in their experiments on photolysis in the light from an electric spark. The intensities of light before and after absorption were measured bolometrically. Hydrogen iodide in hexane (0.08—1.16 M solution) follows Einstein's law. For the aqueous solution, contrary to the equivalence law, the quantum yield decreases for increasing wavelengths of the light source, and for decreasing normality of the solution. The anomaly of the wavelength of the source has been explained as due to the formation of hydrates of hydrogen iodide in the aqueous solution.⁴

Discussing the possible explanation of the observed quantum yield of two molecules, Warburg suggested that HI is decomposed into atoms on illumination, and that the atoms formed could react in one of the following ways:

- (1) $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$
- (2) $\text{I} + \text{HI} \rightarrow \text{I}_2 + \text{H}$
- (3) $\text{H} + \text{H} \rightarrow \text{H}_2$
- (4) $\text{H} + \text{I} \rightarrow \text{HI}$
- (5) $\text{I} + \text{I} \rightarrow \text{I}_2$

However, not all these reactions are equally probable. Warburg calculated the thermodynamic possibility of some of these reactions, and concluded that reactions (1) and (5) are possible, whilst the probability of the reactions (3) and (4) is very small, since the concentrations of the atoms are very small, and reaction (2) is thermodynamically impossible. The final result is that two HI molecules are decomposed per absorbed quantum, and this conclusion is in good agreement with what was observed by Warburg. Nernst and Noddack (*Sitzb. Preuss. Akad.* 110 (1923)) pointed out that thermodynamics can predict only the possibility of a reaction, but not its actual happening.

Stern and Volmer (*Z. wiss. Phot.* **19**, 275 (1920)) represent the reaction mechanism by the following sequence of reactions, where HI' refers to an activated molecule:



Recently, the study of the absorption spectrum of HI by Tingey and Gehrke (*J. Amer. Chem. Soc.* **48**, 1838 (1926)) and Bonhoeffer and Steiner (*Z. physik. Chem.* **122**, 287 (1926)) appears to make possible a decision between the views of Warburg and Stern and Volmer.

According to B. Lewis (*Nature* **119**, 493 (1927); *Proc. Nat. Acad. Sci.* **13**, 720 (1927)), the quantum efficiency in the photochemical decomposition of hydrogen iodide at a pressure of 0.1 mm. of mercury is about two (2.36 in 2080 Å and 2.25 in 2530 Å). Hence it is assumed that Warburg's mechanism is substantiated, and a polar molecule may dissociate in a single elementary act.

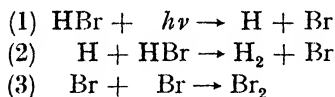
Bonhoeffer and Farkas (*Z. physik. Chem.* **132**, 235 (1927)) have stated that if the first stage in the photochemical decomposition of hydrogen iodide were a molecular excitation, it would be expected that at low pressures fluorescence instead of chemical action would occur. The authors have shown that this is not so, and the law of equivalence is valid down to low pressures. Consequently, it must be assumed that the first stage in the process is a direct dissociation of the molecule into atoms, $\text{HI} \rightarrow \text{H} + \text{I}$. This view finds confirmation in the observation that when the iodide is exposed to light, there is a fall in pressure which can be attributed only to adsorption of free atoms on the walls of the containing vessel. The same experiments also indicate that the iodine molecules formed impede the reaction. Under the action of light, it appears that hydrogen atoms may become detached from the surface of solid hydrogen iodide.

B. Lewis (*J. Phys. Chem.* **32**, 270 (1928)) has shown that under very low pressures, when the collision frequency is comparable with the mean life of the excited molecule, the quantum yield of the photolysis of hydrogen iodide is two. Hence Lewis also supports the view that, on illumination, a molecule of hydrogen iodide is first dissociated by light absorption without the necessity of a collision. Moreover, the continuous spectrum shows dissociation to take place into a normal hydrogen atom and an excited atom of iodine in the metastable 2 P state, an excess energy being dissipated as kinetic energy. The time which elapses between absorption and dissociation is about 2×10^{-10} sec.

DECOMPOSITION OF HYDROGEN BROMIDE. — This reaction was first studied by Coehn and Stuckard (*Z. physik. Chem.* **91**, 722 (1916)) at 270°, in the light of a mercury lamp, who showed that light transmitted by quartz causes a quantitative decomposition of HBr. Warburg studied this reaction in nearly monochromatic radiation, and measured the energy absorbed. The partial pressure of HBr was varied from 20 to 324 mm., and mixtures of H₂ and HBr at atmospheric pressure were used for experiments at room temperature. The light intensity was varied in the different experiments in the ratio 1 : 3 : 7. Because the light absorption of hydrogen bromide becomes too weak for wavelengths higher than 2600 Å, Warburg had to carry on his experiments between 2090 and 2530 Å. As in the case of HI, the velocity of decomposition of HBr in each of these wavelengths was found to be entirely determined by the amount of absorbed light energy, and to be independent of other variables. Also, the quantum yield was again found to be equal to two, as shown in the following table:

Wavelength	2090 Å	2530 Å
$\frac{\text{Mols decomposed}}{\text{Calories absorbed}} \times 10^5$		
Found	1.53	1.79
Calculated . . .	0.735	0.89
Ratio	2.08	2.01

Warburg discussed this reaction, as already outlined in the case of HI, and suggested the following mechanism:



The results of thermodynamic calculations of Warburg exclude the possibility of the reaction (4) $\text{Br} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}$. The reactions (5) $\text{H} + \text{H} \rightarrow \text{H}_2$ and (6) $\text{H} + \text{Br} \rightarrow \text{HBr}$ are unlikely, because of the low concentration of hydrogen atoms. Stern and Volmer preferred to explain the reaction kinetics by assuming the formation of excited hydrogen bromide molecules, and their subsequent reaction on collision. On the other hand, Tingey and Gehrke (*J. Amer. Chem. Soc.* **48**, 1838 (1926)) observed no indication of absorption bands in the continuous absorption spectrum of HBr, and therefore favoured the mechanism of Warburg.

DISSOCIATION OF ALKALI HALIDES.

Recent investigations on the action of light on vapours of different alkali halides have led to results of general importance in the treatment

of photo-kinetics, and in the interpretation of the decompositions of HBr and HI. Terenin (*Z. Physik.* **37**, 98 (1926)) was the first to notice that sodium iodide vapour, at low pressures, emits the first sodium resonance (D) lines when illuminated by light of wavelengths shorter than 2500 Å. Under illumination by wavelengths 1844—1862 Å, the second resonance lines of sodium (3306—3302 Å) also appear in the fluorescence spectrum. Similarly Kondratjew (*Z. Physik.* **39**, 191 (1926)) observed that vapour of caesium iodide emits the second resonance line (4556 Å) of caesium, when illuminated by light of wavelengths 1844 to 1862 Å. He also showed that the life period of the activated sodium iodide molecules, formed by the absorption of light, is short in comparison with the average time between molecular collisions, and that the intensity of the fluorescence is proportional to the amount of absorbed light energy, being independent of the frequency of collision. From these spectroscopic and kinetic observations Kondratjew concluded that alkali iodides are dissociated into a normal iodine atom, and an excited alkali atom, on absorption of light energy, without the intervention of secondary molecular collisions. Moreover, the frequency of the absorbed radiation determines the quantum state of the excited alkali atom, according to the energy relation:

$$h\nu \geq \text{Energy of dissociation} + \text{Energy of excitation (A)}.$$

It might be objected that this interpretation of the experimental results is not in agreement with Franck's views on the impossibility of dissociation of polar molecules (ionically bound) into atoms. However, Hund (*Z. Physik.* **40**, 742 (1927)) has shown from theoretical considerations that absorption of light by ionically bound polar molecules may lead to the removal of the valency electron from the anion to the cation, the result being the formation of neutral atoms and not ions, if sufficient quantum energy of oscillation is supplied, and the molecule is dissociated. Moreover, in contradistinction to the behaviour of homopolar molecules, which will dissociate only when the energy of the absorbed light is sufficiently high to produce one excited and one normal atom, in the case of the ionically bound molecules dissociation will occur even when the energy supplied by absorption of light is so low that two normal atoms are formed. Recently Franck, Kuhn, and Rollefson (*ibid* **43**, 155 (1927)) observed that the absorption spectra of the vapours of the alkali halides are wholly continuous, without any indication of a band structure. In the spectral region 4000—2300 Å, the chlorides were found to have one absorption maximum, bromides two, and iodides two, and a beginning of a third extending to shorter

wavelengths. The authors assumed that the continuous bands which are situated on the long wavelength side of the absorption spectra correspond to the dissociations of the molecules into two normal atoms. The second bands are likely to indicate the occurrence of dissociation into an excited halogen atom and a normal alkali atom, because excitation of alkali atoms would require considerably more energy, and the corresponding bands should lie in the ultra-violet, as indicated by the presence of the third band in the spectra of the alkali iodides. In the following table the results obtained by Franck and co-workers, Terenin and Kondratjew, on the energy changes with alkali halides are recorded:

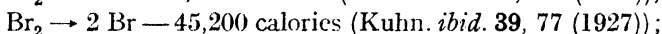
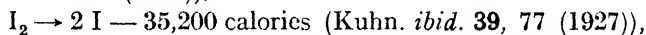
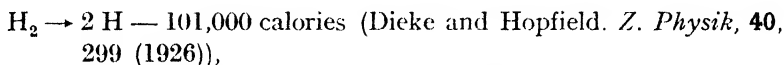
1	2	3 Å	4 $N h \nu$	5 $N (h \nu_1 - h \nu_2)$	6	7
			Calories	Calories	Calories	Calories
	Na + I	> 3900;	73000		< 73000	63000
NaI	Na + I*			22600	$2^2P_2 - 2^2P_1 = 21500$	
	Na* + I	2500;	114000		$I S - 2 P = 48000$	63000
	Na* + I	> 1862;	< 153000		$I S - 3 P = 86000$	63000
CsI	Cs + I	3800;	75000			
	Cs* + I	> 1862;	< 153000		$I S - 3 P = 62400$	75000
KI	K + I	3800;	75000		< 90000	75000
					< 75000	84000
NaBr	Na + Br	3100;	91000	9300	$2^2P_2 - 2^2P_1 = 10400$	91000
	Na + Br*					84000
KBr	K + Br	3100;	91000	8500	$2^2P_2 - 2^2P_1 = 10400$	91000
	K + Br*					100000
RbBr	Rb + Br*			8700	$2^2P_2 - 2^2P_1 = 10400$	103000
	Na + Cl	2800;	103000		$2^2P_2 - 2^2P_1 = 2500$	
NaCl	Na + Cl*			—		

The second column in the above table represents the process occurring on light absorption, the excitation of an atom being indicated by an asterisk; the third column denotes the long wavelength side of the corresponding band in Å units, and the $Nh\nu$ values in calories, whilst the fourth represents the energy difference ($N(h\nu_2 - h\nu_1)$) between the absorption maxima of the first and the second alkali halide bands in the experiments of Franck and co-workers, and this is approximately equal to the excitation energy of the halogen atoms. The fifth column represents the atomic excitation energies calculated from spectroscopic data, and finally the 6th and 7th columns compare the heats of dissocia-

tion of alkali halides into normal atoms, as calculated from the experiments of Franck and co-workers by the equation (A), and as determined from the thermochemical data.

The agreement of the figures in columns 4 and 5, and 6 and 7 respectively is satisfactory, and these energy calculations support the views of Franck and his co-workers.

On the other hand, this simple relation between the long wavelength limit of the absorption spectra and their heats of dissociation is not applicable to the hydrogen halides. The heats of dissociation of the hydrogen halides can be calculated with considerable precision, because the heats of dissociation of H_2 and I_2 and Br_2 molecules are accurately known:



but the continuous absorption of HI ceases at 3200 \AA ($Nh\nu = 89,000 \text{ cal.}$), and that of HBr between 2600 and 2800 \AA ($Nh\nu = 109,000$ to $101,000 \text{ cal.}$). Similar disagreement between the limits of continuous spectra and the heat of dissociation determined thermochemically was observed by Franck and Kuhn (*Z. Physik.* **43**, 164; **44**, 607 (1927)) with iodide, bromide, and chloride of silver. In these cases the heat of dissociation calculated from the limits of their continuous absorption spectra is higher than that determined thermochemically. To explain this discrepancy, Franck and Kuhn suggest that these molecules, although polar, are not composed of ions but of atoms, and believe that this view is supported from researches on the optical and electrical properties of the silver halides in the solid and molten states. It has already been pointed out that molecules, of which atoms and not ions are the oscillating parts, can be dissociated on light absorption only if one or both of the atoms produced are in the excited state. Franck and Kuhn assume therefore that silver halides are dissociated into a normal silver atom and an excited halogen atom, and find better agreement with the observed thermochemical data. On applying the same mechanism to the case of the hydrogen halides, and suggesting that the nature of the binding is of the atomic type, Franck and Kuhn observed the following values with hydrogen iodide: $Nh\nu \text{ abs} - Nh\nu \text{ excited} = Q \text{ dissociation} = 89,000 - 21,500 = 67,500 \text{ cal.}$, instead of the experimental value $69,000 \text{ cal.}$ In the case of HBr the calculated value is $98,600 \text{ cal.}$, whilst the thermochemical value is $85,000 \text{ cal.}$ (compare Franck. *Ber.* **61**, B, 445 (1928)).

Kondratjew (*Z. Physik.* **48**, 583 (1928)) has indicated that hydrogen iodide is a homopolar molecule, because hydrogen iodide, on absorption of light of a suitable wavelength, yields a hydrogen atom and an excited iodine atom. In the cases of hydrogen chloride and hydrogen bromide, the dissociation energies, calculated from the infra-red vibration spectra according to the method of Franck and Kuhn (*loc. cit.*), are shown to be in good agreement with the values obtained from the thermochemical data. Hence it is concluded that the molecules of all the hydrogen halides are homopolar in character (compare Debye — *Polar Molecules, Chemical Catalog Company, New York*, page 59 (1929)).

FORMATION OF OZONE.

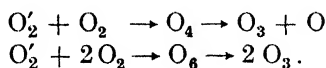
Lenard (*Ann. Physik* **1**, 486 (1900)) found that at ordinary gas pressures only the extreme ultra-violet radiation—below 2000 Å—causes the ozonization of oxygen. Regener (*Ann. Physik.* **20**, 1033 (1906)) showed that a stationary state is gradually reached with a small percentage of the total oxygen present as ozone, under the influence of the total radiation of a spark discharge, and that ozone is decomposed mainly by the action of wavelengths longer than those of the extreme ultra-violet.

Contrary to previous observations, Warburg (*Sitz. Akad. Wiss.* **216** (1912); **872** (1914); *Z. Elektrochem.* **27**, 133 (1921)) showed that ozone can be formed by the action of radiation of a much longer wavelength than 1900 Å, provided oxygen under high pressure is used, and thereby a sufficient light absorption secured. In the following table Warburg's results on quantum yield at different oxygen pressures and wavelengths are recorded:

	95% O ₂ ; 5% N ₂	Air 21% O ₂ and 79% N ₂	
Pressure kg/cm ²	47.5, 99—100, 100—140, 300	136—146	293
Wavelength	Quantum yield	Quantum yield	
2070 Å	1.03 0.92 0.91 0.77	0.93	0.65
2530 Å	— 0.63 0.55 0.29	—	—

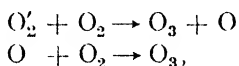
A quantum yield of unity would indicate the formation of two ozone molecules on absorption of one quantum of light energy, according to the equation: $O_2 + h\nu + 2O_2 \rightarrow 2O_3$. The table shows, however, that only in the light of mean wavelength 2070 Å, and under pressures not exceeding 100 atmospheres, the quantum yield is very close to unity. With increasing pressure, the yield drops steadily. More pronounced still is the drop of the quantum yield in the wavelength region 2530 Å.

Here, even at low pressures, considerably less than two molecules of ozone are formed per quantum of light energy absorbed. In the opinion of Warburg, who assumed the primary process, on illumination, to be a dissociation of the oxygen molecule into atoms, the deviations of the quantum yield from unity are due mainly to two causes. The smaller yield, in light of the average wavelength 2530 Å, is due to the energy quanta being smaller than the heat of dissociation of oxygen molecules (taking 140,000 calories for heat of dissociation of oxygen molecules). On this view, activated molecules, and not atoms, are produced by this wavelength, and hence the yield is likely to be less than unity. The decrease of the quantum yield at higher oxygen pressures is caused by the taking up of the absorbed energy of the activated molecules by the neighbouring inactive molecules.¹ This view of Warburg is supported by his observation that there is deviation from Beer's law with oxygen, and that the absorption coefficient of oxygen for radiation of wavelength 2070 Å increases only 6.8 fold when the pressure is raised from 27.5 to 322.5 kg/cm². A similar though less marked increase was observed for wavelength 2530 Å. Recently, Eucken (*Z. physik. Chem.* **107**, 436 (1923)), working with extreme ultra-violet radiation (1862—1719 Å), observed that the yield of ozone at atmospheric pressure of oxygen is practically independent of temperature, and that at concentrations less than 5×10^{-3} mols per litre, there is much more rapid ozone formation at liquid air temperature than at room temperature. Such negative temperature-coefficient of ozone formation is explained by Eucken on the assumption that the mean life of the activated molecules, formed on illumination, depends on the temperature of the gas.¹ These activated molecules either react on collision, or lose the energy of activation by re-emission of the absorbed radiation. Eucken imagines the following processes on collision:



A recent study of the absorption spectrum of oxygen by Birge and Sponer (*Phys. Rev.* **28**, 259 (1926)) seems to support Eucken's assumption that activated molecules, and not atoms, are formed on illumination. According to Birge and Sponer, only light below wavelength 1751 Å atomises a molecule of oxygen into a normal and an excited oxygen atom. The heat of dissociation of oxygen molecules into normal atoms is not much less than 162,000 calories, and hence, if the dissociation of oxygen molecules into two normal atoms is a general phenomenon on illumination, it cannot be caused by light of wavelength employed by

Warburg in his experiments. The energy quanta of wavelength 2070 Å correspond to 140,000 calories per mol, and those of wavelength 25,000 Å correspond to 112,000 calories. Thus it must be concluded that the difference in the quantum yields for these two wavelengths may only be due to the difference in the energy contents of these activated molecules. It is probably impossible for ozone to be formed by a trimolecular collision, according to the equation: $O_2' + 2 O_2 \rightarrow 2 O_3$; since, instead of a decrease, an increase of the quantum yield with pressure would have been anticipated in the case of such a possibility. On the other hand, if the reaction is



the decreasing yield in wavelength 2530 Å can be attributed to the activation energy being slightly smaller than, or equal to, the heat of this process* (approximately 113,000 cal., if $O_2 \rightarrow 2 O$ requires 162,000 cal.), so that only a fraction of all the collisions of activated molecules is successful.

DECOMPOSITION OF AQUEOUS SOLUTION OF POTASSIUM NITRATE.

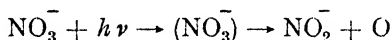
The decrease of the quantum yield is particularly noticeable in several photochemical reactions occurring in aqueous solutions. The results of earlier researches (Thielard, *Ber.* **40**, 4914 (1907); Lombard, *Compt. rend.* **150**, 228 (1910); Berthelot and Gaudechon, *ibid.* **152**, 522 (1911); Baudisch *Ber.* **44**, 1009 (1911)) showed that nitrite and molecular oxygen are formed when an aqueous solution of potassium nitrate is exposed to ultra-violet light. Dhar and Sanyal (*J. Phys. Chem.* **29**, 926 (1925)) showed that the same reaction takes place in tropical sunlight: $2 KNO_3 \rightarrow 2 KNO_2 + O_2$. Warburg's experiments (*Sitzb. Preuss. Akad. Wiss.* 1228 (1918)) showed that the rate of decomposition is much faster in alkaline than in acid solutions of nitrates. Warburg's results are recorded below:

0.0033 N NaOH			
Wavelength concentration	2070 Å	2530 Å	2820 Å
0.33 N KNO ₃	0.25	0.17	0.024
0.033 N KNO ₃	0.19		
0.0033 N KNO ₃	0.10		

These results of Warburg were questioned by Anderson (*J. Amer. Chem. Soc.* **46**, 797 (1924)), but later on substantiated and extended by Villars (*ibid.* **49**, 326 (1927)). The results of Villars are represented below:

	KNO ₃		1.0 N		$p_H = 9.9$		
Wavelength Å	2540	2700	2800	3020	3130	3350	3660
Quantum yield	0.30	0.07	0.024	0.013	0.010	0.014	0.

The quantum yield falls off very rapidly at wavelengths above 2500 Å. According to Warburg, the chemical process which follows on absorption of radiation by nitrate ions takes place according to the scheme:



This process requires about 95,000 calories corresponding to wavelength 2800 Å to 3150 Å. To account for the small quantum yield, Warburg suggested that the activated NO_3^- ions lose their energy before reacting by inelastic collisions. From Villars' data we find that the reaction proceeds at a measurable speed even in presence of radiation longer than 3150 Å, which is the minimum frequency as calculated by Warburg for his scheme. Hence it is clear that some other process is also involved in the photochemical decomposition of potassium nitrate. Moreover, the influence of H ion concentration on the quantum yield can hardly be accounted for by Warburg's suggestion that the undissociated nitric acid molecules are less easily decomposed photochemically than the nitrate ions. The rapid decrease of the quantum yield with decrease in the concentration of nitrate is difficult to explain.

DECOMPOSITIONS OF AMMONIA AND HYDRAZINE.

Ammonia shows a marked absorption of light below 2260 Å (Leifson, *Astrophys. J.* **63**, 73 (1926)). Warburg (*Sitzungsb. Preuss. Akad. Wiss.* **746** (1911), **216** (1912)) investigated this reaction, and concluded that in absence of oxygen ammonia decomposes on illumination into nitrogen and hydrogen according to the equation: $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$. Warburg found the quantum yield of the decomposition in radiation of 2025 to 2140 Å at room temperature to be 0.25, and this value remains unchanged on variation of NH_3 concentration, or by the addition of large amounts of a mixture of N_2 and H_2 in the proportion of 1:3. Thus the reaction is not retarded by its decomposition products, and no stationary state is being formed on prolonged illumination. This latter con-

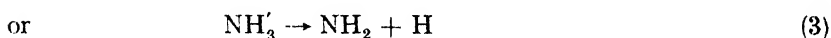
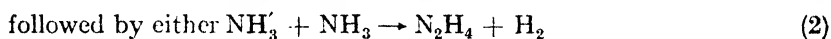
clusion was confirmed by Coehn and Pringent (*Z. Elektrochem.* **20**, 275 (1914)). Kuhn (*Compt. rend.* **177**, 956 (1923); **178**, 708 (1924); *J. Chim. phys.* **23**, 521 (1926)) found the quantum yield to be independent of the pressure of ammonia within wide limits (5 to 300 mm.), and an exact doubling of the gas pressure was obtained on total decomposition of a sample of ammonia. The rate of reaction was found to be proportional to the incident light intensity; but the absolute values of quantum yields differ considerably from those of Warburg. Kuhn further reported that by increasing the monochromatic nature of the radiation, using, instead of a group of zinc lines between 2025—2140 Å, only two lines, 2063 and 2100 Å,—the quantum yield can be decreased from 0.45 to 0.10. Moreover, Kuhn observed that the quantum yield increased about 50% for every 100° temperature increase, reaching a 7 fold value at 500°. Kuhn advanced the view of the reaction mechanism which assumes that only a fraction of the ammonia molecules, which absorb light energy, decompose. The primary photochemical process is assumed to be a unimolecular decomposition: $\text{NH}_3 \rightarrow \text{N} + \text{H} + \text{H}_2$. A series of secondary reactions are supposed to account for the observed variations in the quantum yield. Bates and Taylor (*J. Amer. Chem. Soc.* **49**, 2438 (1927)), however, have pointed out that the primary process of the type suggested by Kuhn appears impossible according to the recent data on the heats of dissociation of nitrogen and hydrogen molecules, since the process suggested by Kuhn requires about 60,000 calories more than is supplied by the absorbed quanta.

It has been suggested that all ammonia molecules are decomposed on light absorption, either in a bimolecular reaction: (1) $\text{NH}_3' + \text{NH}_3 \rightarrow \text{N}_2\text{H}_4 + \text{H}_2$ or unimolecularly (2) $\text{NH}_3' \rightarrow \text{NH}_2 + \text{H}$. The following secondary reactions can also take place: (3) $\text{H} + \text{H} \rightarrow \text{H}_2$, (4) $\text{NH}_2 + \text{NH}_3 \rightarrow \text{N}_2\text{H}_4 + \text{H}$, (5) $\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}$. At room temperature hydrazine is probably decomposed only photochemically, but at higher temperatures, a thermal reaction may take place. This would partly explain the increased quantum yield at higher temperatures. It should be pointed out that Bates could not detect any change in the absorption spectrum of ammonia on long illumination, showing the absence of a substance of high light absorption coefficient. The point which is unquestionably established by the more recent studies on ammonia decomposition is that its mechanism, although apparently so simple at room temperature, is in reality, quite complicated.

It appears therefore that no mechanism has as yet been proposed for this reaction which is in complete agreement with experimental facts, nor has the primary process been established beyond doubt. The

simple reaction of an activated ammonia molecule on collision with a normal one to yield nitrogen and hydrogen, $\text{NH}_3' + \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$, does not account for the small quantum yield at high pressures, nor the observation of Bonhoeffer and Farkas (*Z. physik. Chem.* **134**, 337 (1928)) that a rapid decomposition takes place at a pressure of 0.001 mm. of mercury. Photochemical decomposition is expected to stop, and fluorescence should appear at this low pressure. The ultra-violet absorption bands of ammonia, also, do not show the fine structure ordinarily expected for cases where light absorption leads only to the activation of the molecule.

From considerations based on the facts that ammonia is decomposed by excited mercury atoms with an energy content of 112,000 calories, and that the gaseous products of the reaction contain hydrogen in excess of the stoichiometric proportion $\text{N}_2 : 3 \text{H}_2$, Bates and Taylor (*J. Amer. Chem. Soc.* **49**, 2438 (1927)) have proposed the following mechanism:



The hydrazine formed will undergo a secondary photochemical change into nitrogen and hydrogen.

Recently Elgin and Taylor (*J. Amer. Chem. Soc.* **51**, 2059 (1929)) have shown that gaseous hydrazine is decomposed by ultra-violet light and by excited mercury atoms. They have shown that the decomposition velocity by optically excited mercury atoms is greater than that with radiation from a quartz mercury arc. The products of the reaction in both cases are ammonia, nitrogen, and hydrogen, in amounts indicating a reaction according to the equation $2 \text{N}_2\text{H}_4 \rightarrow 2 \text{NH}_3 + \text{N}_2 + \text{H}_2$. The ammonia formed also decomposes under the action of light.

The products from the thermal decomposition of gaseous hydrazine in a quartz bulb indicate a reaction mainly according to the equation $3 \text{N}_2\text{H}_4 \rightarrow 4 \text{NH}_3 + \text{N}_2$. The thermal reaction appears to be heterogeneous and unimolecular in character.

The pure photochemical reaction is not affected by the increase of temperature, or by the presence of large concentrations of ammonia or hydrogen. The photochemical decomposition of ammonia proceeds at

a velocity which is one-tenth of that of hydrazine under identical conditions.

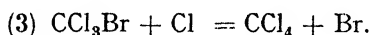
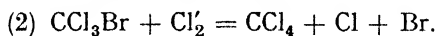
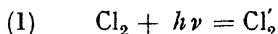
Elgin and Taylor state that the mercury sensitised hydrazine decomposition is a very rapid reaction. Its velocity is nearly 40 times that of ammonia under identical conditions. The sensitised decomposition of hydrazine shows a minimum quantum yield of 13 molecules decomposed per quantum absorbed, and it appears to be a chain reaction. The velocity of the sensitised reaction is unaffected by the presence of nitrogen, ammonia, or hydrogen in large concentrations. That hydrogen does not retard the reaction is probably due to the interaction of hydrogen atoms with hydrazine. The velocity of the sensitised decomposition of hydrazine appears to be directly proportional to the intensity of the incident light.

From measurements of the absorption spectrum of gaseous hydrazine, Elgin and Taylor report that ultra-violet rays below 2440 Å are appreciably absorbed by gaseous hydrazine. The absorption spectrum consists of a series of faint, apparently continuous bands, followed by a region of continuous absorption. The above authors explain their results by a reaction mechanism based upon a dissociation of the primarily excited molecule as a primary process, and not one involving an activated molecule, and they state: "The spectral evidence offered by the hydrazine absorption spectrum is not entirely conclusive. It is, however, in accord with our suggested mechanism, if we accept the Bonhoeffer and Farkas conclusion (*Z. physik. Chem.* **134**, 337 (1928)) concerning the process giving rise to a spectrum consisting of continuous bands. Indeed, we may state that if it can be conclusively shown that the hydrazine bands do not possess a fine structure, our results provide strong evidence in support of this idea concerning the Henri 'predissociation spectra', (V. Henri, *Structure des Molecules*, Librairie Scientifique. J. Hermann, Paris (1925)). A study of the photochemical decomposition of methylamine, which has been definitely shown by Henri to possess a spectrum of this type, should prove of interest in this connection."

RESEARCHES OF NERNST AND HIS PUPILS ON THE LAW OF EQUIVALENCE.

Starting with the assumption that the primary action of light on halogens results in the dissociation of their molecules into atoms, Nernst suggested that in presence of suitable acceptors, the atoms formed would react quantitatively, yielding two molecules of the reaction product per quantum. In his laboratory, several reactions of this type were studied. Miss

Pusch (*Z. Elektrochem.* **24**, 336 (1918)) investigated the photobrominations of toluene, heptane, hexane, and hexahydrobenzene vapours in radiations of wavelengths 4400—5300 Å obtained from a "Nitra" lamp (nitrogen filled), and observed an approximate confirmation of the views of Nernst regarding the last reaction; whilst the other processes yielded as many as 20 molecules per quantum absorbed. Hydrogen Miss Pusch finds to be an unsuitable acceptor in its reaction with bromine, the amount of change observed being much less than that expected from theory, since with sunlight in one experiment 0.02 gr. bromine combined with hydrogen instead of 2.3 grs. Noddack (*ibid.* **27**, 359 (1921)) confirmed the results of Pusch for the bromination of hexahydrobenzene, that one molecule of bromine reacts per quantum absorbed. Noddack (*loc. cit.*), and later Grüss (*Z. Elektrochem.* **29**, 144 (1923)), using radiations of wavelengths 3910—4400 Å and 4400—4680 Å, studied the rate of chlorination of CCl_3Br by dissolved chlorine, under the action of light absorbed by the latter. The rate of reaction in pure CCl_3Br , as measured by Noddack, corresponded to one molecule of chlorine reacting per absorbed quantum. The admixture of carbon tetrachloride decreased the quantum yield of the reaction. Noddack suggested that activated chlorine molecules are formed by absorption of light energy, and are then deactivated in dilute solutions before they collide with CCl_3Br molecules to react according to the scheme:



Grüss showed, however, that using thoroughly purified CCl_4 and SiCl_4 , the reaction proceeded at the rate of one molecule of chlorine per quantum absorbed, even in dilute solutions containing an excess of SiCl_4 or CCl_4 . The retardation observed by Noddack was ascribed to impurities. Grüss suggested that the life period of the activated molecules is of the order of 10^{-7} sec., and that almost all collisions with CCl_4 and SiCl_4 are elastic. It will be interesting to note here that Miss von Ranke (*Z. Elektrochem.* **27**, 361 (1921)) has reported that the reaction also takes place in the dark at high temperatures, and is not trimolecular but is bimolecular. Hence it appears that in the dark the same mechanism is observed as that suggested by Noddack in presence of light.

The oxidation of CCl_3Br according to the equation $2 \text{CCl}_3\text{Br} + \text{O}_2 = 2 \text{COCl}_2 + \text{Cl}_2 + \text{Br}_2$ has also been studied by Grüss (*Z. Elektrochem.* **29**, 144 (1923)) in CCl_4 solutions. The velocity of this reaction is independent of the concentrations both of CCl_3Br and oxygen. Bromine behaves as an optical sensitizer, and for one quantum of light absorbed, two molecules of CCl_3Br are oxidized.

CAUSES OF THE INAPPLICABILITY OF THE EINSTEIN LAW.

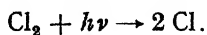
The Einstein law is certainly too narrow to embrace all photochemical phenomena in all their complexities. The law simplified the problem too much, in neglecting certain influences which may be highly important. However, the verifications, which have been observed in the case of several reactions, show that the number of quanta absorbed by a photosensitive substance is an essential factor determining the quantity of matter transformed. These verifications justify the opinion that the law of equivalence is applicable in some ideal cases, and can serve as a basis of the theory of photochemical phenomena.

Causes which diminish the quantum yield. — Between the instant when a molecule absorbs light and that when it is chemically transformed, whether alone or reacting with another molecule, there is always a certain interval of time. During this time the molecule can lose its activity by giving up the quantum absorbed, either as heat or as radiant energy. It is clear that the photochemical yield will be small if the phenomenon of deactivation is very frequent. This loss of activity is never spontaneous. Collision with other molecules, or simply the neighbourhood of other molecules, can accelerate this loss of activity. The molecules of the solvent may also accelerate the deactivation. This is how Warburg (*Sitzungsb. d. Preuss. Akad. d. Wiss.* **1229** (1918)) explained the small quantum yield with substances in solution, specially in the photochemical decomposition of an aqueous solution of potassium nitrate. However, there are cases where the influence of the solvent is not manifest and the law of equivalence is verified, and there is no decrease of quantum yield with decrease of concentration. It may be concluded that such observations lead to the estimation of the life period of activated molecules. The reaction between chlorine and CCl_3Br follows the law of equivalence up to the concentration $M/50$, and Grüss concluded that the life period of activated molecules is of the order of 2×10^{-7} sec., whilst in presence of bromine the life period becomes 1.5×10^{-7} sec. Similarly, the life period of active chlorine molecules in the sensitized decomposition of

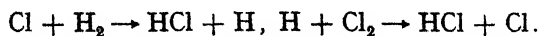
ozone by the presence of chlorine, even when the partial pressure of ozone is very small, has been found to be of the order 10^{-7} sec.

It is remarkable that in these reactions the molecule, after absorbing a quantum, remains in the active condition till its encounter with the molecule of the acceptor, although before this encounter there are numerous collisions with other molecules. It can also be conceived that the activity communicated by light to a photosensitive molecule allows it to enter into reaction only with the molecules of the acceptor possessing an internal energy greater than a certain limit. The molecules of the acceptor which are capable of reacting would be more numerous as the temperature is increased. Consequently, a thermal acceleration is observed. It should be emphasized that the molecules of a gas or liquid are not in the same state of activation at a fixed temperature, and hence they are not equally activated on light absorption. The opinion has been expressed that a quantum of a given frequency can activate only those molecules which are least removed from the critical state, and of which the energy is greater than the mean energy. As these active molecules are extremely few in number in the total mass, the quantum yield is likely to be very small, at least this would be an important factor in the decrease of the quantum yield, unless some other cause leads to an increase of the quantum yield. It has been repeatedly stated that "the law of equivalence is not applicable to the total reaction," but is only applicable to the primary process. But this view seems untenable from the foregoing considerations.

Principal causes which lead to increase of photochemical yield. — There are numerous photochemical reactions which proceed even in the dark at a speed greater than the ordinary thermal velocity after illumination. In other words, these reactions show the phenomenon of photochemical "after effect". It appears that in such cases the increased quantum yield may be due to the formation of a catalyst. In other changes, increased quantum yield has been explained from the view point of chain formation, which was first introduced by Nernst (*Z. Elektrochem.* **24**, 335 (1918)) to explain the large quantum yield in the photosynthesis of HCl. According to Nernst a molecule of chlorine is dissociated into atoms on absorption of a light quantum.



This dissociation is followed by two secondary reactions which are repeated alternately a large number of times:



The quantity of matter transformed by a single quantum appears to be unlimited under this scheme. But other reactions in which catalysts are likely to play an important part are supposed to take place: — $2\text{Cl} \rightarrow \text{Cl}_2$; $\text{Cl} + \text{H} \rightarrow \text{HCl}$, $2\text{H} \rightarrow \text{H}_2$; and these reactions break up the chain of reactions previously discussed. In reality this hypothesis of Nernst in all its simplicity cannot explain all the observed facts in the photosynthesis of HCl . However, the chain mechanism has been extended to numerous other photochemical (as well as to thermal) reactions by different investigators.

Bodenstein (*Z. phys. Chem.* **85**, 329 (1913)) expressed the opinion that the primary phenomenon produced by light is the ionization of the photosensitive substance, and that the electrons liberated combine with other molecules, which are thus activated. This view has been given up by Bodenstein himself.

In order to explain the abnormally large photochemical yield in such exothermal reactions as the combination of hydrogen and chlorine, decompositions of hydrogen peroxide, ozone etc., Dhar and collaborators (*J. Phys. Chem.* **28**, 948 (1924); *Z. anorg. Chem.* **159**, 103 (1926)) suggested the following explanation:

Apart from the well known researches of Richardson and co-workers (*Phil. Trans. A.* **222**, 1 (1921), *Proc. Roy. Soc. A* **115**, 20 (1927)), the results obtained by Haber and Just (*Ann. Physik* (4), **36**, 308 (1911)), Pinkus (*J. Chim. physique* **18**, 336, 412 (1920)), Bloch (*Compt. rend.* **150**, 694 (1910)), Tanatar and Burkser (*J. Russ. Phys. Chem. Soc.* **45**, 1 (1913)), Potter (*Proc. Roy. Soc. B.* **91**, 465 (1915)), Brewer (*J. Amer. Chem. Soc.* **46**, 1403 (1924)), Henry (*J. Phys. Chem.* **33**, 1941 (1929)), and others, show definitely that ionization takes place in all the exothermal reactions investigated by the above workers. Moreover, we have obtained evidence of the generation of ions in the slow oxidation of sodium and sodium sulphite in air. Recently, Finch and Stimson (*Proc. Roy. Soc. A* **116**, 379 (1927); *A* **124**, 356 (1929)) have shown that when mixtures of gases like hydrogen and oxygen, carbon monoxide and oxygen, are adsorbed by the surfaces of gold and silver, the metal surfaces become charged. It seems likely that ionization takes place during the process of adsorption, which is possibly chemical in nature. If proper precautions are taken, and the ionization is measured before a good deal of recombination occurs, we are likely to get evidence of ionization in most exothermal chemical changes. It is well known that the photochemical decomposition of H_2O_2 , and the combination of H_2 and Cl_2 , are highly exothermic chemical changes, and that Einstein's law of photochemical equivalence is not applicable to these cases, since many mole-

cules decompose or react per quantum absorbed. We have advanced the view that ionization takes place when these substances decompose, or react on illumination, and the ions generated are absorbed by the inactive molecules, which are now activated even in the absence of light; and consequently the amount of chemical change is greater than corresponds with the amount of light absorbed. Moreover, Ludlam has observed that humidity, which frequently acts as a catalyst in reactions involving chlorine, also favours its ionization.

Most of the photochemical reactions, as has already been stated, are exothermal, and the energy given out in the transformation of the molecules caused directly by light absorption is transmitted to other molecules, which are thus rendered active. Let q be the energy given out in the reaction between a molecule of chlorine and a hydrogen molecule in the dark. If the molecule of chlorine has been previously activated by light, the heat given out becomes $q + h\nu$. This energy, which is greater than $h\nu$, is sufficient for activating a second molecule of chlorine, which on reacting, liberates again a quantity of energy sufficient for activating a third molecule, and so on. A single quantum thus causes the formation of an unlimited amount of HCl, if the energy of the chemical reaction is not at all dissipated away.

We have already given a picture of the mechanism by which the liberated energy is transmitted from one molecule to another, from the view point of the generation of ions in exothermal chemical reactions. On the other hand, Baly (*J. Chem. Soc.* **119**, 653, 1025 (1921)) advanced the view that the energy is given out as infra-red radiations, which are absorbed by the photosensitive substance, and thus activate it. This supposition seems incorrect, because infra-red radiations have little photochemical activity. On the other hand, an emission of radiation of short wavelengths will be manifested by visible fluorescence. As a matter of fact, fluorescence accompanies many photochemical reactions, but it is not characteristic of all highly light-sensitive substances. The experiments of Miss Kornfeld (*Z. phys. Chem.* **108**, 118 (1924)) show that in the photosynthesis of phosgene, for which the quantum yield is very high, radiations capable of passing through quartz are not emitted.

Cario and Franck have brought evidence to show that a molecule which has absorbed a quantum of light can, in certain cases, give up its energy to another molecule with which it comes in contact, and render it active. Certain cases of photosensitization are explained from the above view point. There is no doubt that the energy liberated in a chemical transformation of a molecule can be transmitted to another molecule by collision. The only question is to ascertain whether this

transmission of energy takes place through quanta sufficiently large for the activation of the molecules.

Recently Pinkus and Henry (*Bull. Soc. Chim. Belg.* **37**, 285 (1928)) have shown that at about 300° the mixing of nitric oxide or nitrogen peroxide and oxygen leads to the generation of ionization currents of 10^{-14} to 5×10^{-13} ampere. The ions are shown not to be of thermionic origin. Moreover, Pinkus and Ruyssen (*Ibid.* **37**, 304 (1928)) have stated that by passing ozonized oxygen through an ionization chamber at 220 — 240° , and combining measurements of the ionization current with analyses of the gases entering and leaving the chamber, the decomposition of 10^{-6} to 10^{-7} gram mol. of ozone per second in a field of 845 volts per cm. produces currents of 10^{-11} to 10^{-12} ampere.

Recently Basu (*J. Phys. Chem.* **33**, 1200 (1929)) has suggested that high quantum yield in photochemical reactions may be partly due to the activation of more than one molecule of the absorbing substance by one quantum of the incident radiation.

CHAPTER VI.

Photochemical Reactions with Chlorine as a Reacting Substance.

PHOTOSYNTHESIS OF HYDROCHLORIC ACID.

Cruickshank in 1801 (*Nicholson's Journ.* 5, 202 (1801)) was probably the first to observe the formation of hydrochloric acid from a mixture of hydrogen and chlorine under the action of light. This is undoubtedly the photochemical reaction which has been investigated most, but its mechanism is far from being clear. Amongst the researches carried out in the first half of the last century, one can mention those of Seebeck, Gay-Lussac, Thénard, and Favre and Silberman. In studying this reaction, Draper (*Phil. Mag.* 19, 195 (1841); 23, 401 (1843); 27, 327 (1845)) for the first time stated the proportionality between the photochemical effect and the amount of light received by a system. These measurements were taken up again with great precision and care by Bunsen and Roscoe (1855—1859).

The combination of hydrogen and chlorine is still, after more than half a century, a plentiful source of problems.

The principal facts about this reaction have been summarized as follows by Hinshelwood (*Chemical Change in Gaseous Systems*, p. 76, Oxford 1926).

(1) The reaction is caused by the light absorbed by chlorine.

(2) There may be a long "induction period", during which no change takes place. This has been traced by Burgess and Chapman (*J. Chem. Soc.* 89, 1399 (1906)) to the presence of nitrogenous impurities, which give rise to nitrogen chloride and inhibit the reaction. The inhibitors are gradually destroyed by light, and the combination starts. In their absence the induction period disappears.

(3) The Einstein law is not even approximately obeyed. One quantum of light brings about the union of many millions of molecules.

(4) The actual kinetics of the reaction are very complicated. The rate is inversely proportional to the concentration of oxygen, and appears to increase almost indefinitely as the gases are freed from

oxygen. It is therefore necessary, in making measurements of the reaction velocity, always to work in the presence of a small but definite concentration of oxygen.

(5) The rate of combination increases at first in direct proportionality to the pressure of hydrogen, when the pressure of chlorine and of oxygen is kept constant, then passes through a maximum, and slowly declines as the pressure of hydrogen is further increased.

(6) Bodenstein and Dux (*Z. physikal. Chem.* **85**, 297 (1913)) found that, for constant pressures of hydrogen, the rate of reaction was given by the formula:

$$\frac{d[\text{HCl}]}{dt} = \frac{KI[\text{Cl}_2]^2}{[\text{O}_2]}$$

where I is the intensity of the light and K a constant; whilst Chapman and Whiston (*J. Chem. Soc.* **115**, 1264 (1919)) found it to be more nearly expressed by the formula

$$\frac{d[\text{HCl}]}{dt} = \frac{K \cdot I [\text{Cl}_2]}{[\text{O}_2]}.$$

(7) Mrs. M. C. C. Chapman (*J. Chem. Soc.* **123**, 3062 (1923)) has submitted the matter to a very careful reinvestigation, and finds that the rate of combination is proportional to the first power of the concentration of the chlorine when the proportion of hydrogen present is small, and proportional to the square of the concentration of the chlorine when the proportion of hydrogen present is large. Another important result was that as the pressure of hydrogen becomes smaller the rate of reaction becomes less and less dependent on the oxygen concentration. The results are summarized in the formula:

$$\frac{d[\text{HCl}]}{dt} = \frac{K_1[\text{H}_2][\text{Cl}_2]^2}{K_3[\text{H}_2]^{2-\alpha}[\text{O}_2] + [\text{Cl}_2]},$$

where α is a fraction less than 0.5.

An interpretation of this formula, on the basis of the assumptions that chlorine is activated by light and can be deactivated by the joint action of hydrogen and oxygen, is given by Mrs. M. C. C. Chapman and D. L. Chapman (*J. Chem. Soc.* **123**, 2079 (1923)).

(8) Very complete desiccation prevents the combination of hydrogen and chlorine under the influence of light of the visible region. Early observers had noticed that the hydrogen-chlorine mixture, when thoroughly dried over phosphorous pentoxide, reacts only very slowly in light. Coehn and Jung (*Z. physikal. Chem.* **110**, 705 (1924)) found

that there was no combination in systems where the pressure of water vapour was estimated to be 10^{-7} mm. Hg, no reaction occurred even after 20 days' exposure to sunlight; but that the reaction took place rapidly when the pressure was 10^{-5} mm. Bodenstein and Dux (loc. cit.) had found that variation of the pressure of water vapour between 10 mm. and 10^{-3} mm. had no effect on the combination, and concluded that the non-reactivity of gases dried over P_2O_5 might be due to some inhibition. (Tramm (*Z. physik. Chem.* **105**, 356 (1923)), however, using the modern vacuum technique, and liquid air for freeing both apparatus and gases from moisture, showed that dry gases did not combine at all in visible light.)

(In ultra-violet light, on the other hand, Coehn and Jung found that the thoroughly dried mixture combined as well as the moist mixture.) G. B. Kistiakowsky (*J. Amer. Chem. Soc.* **49**, 2194 (1927)) states that intensive drying of chlorine does not affect the absorption; nor is any appreciable part of the absorbed light re-emitted by fluorescence. Thus it seems hard to believe that water can play any part in the dissociation of chlorine molecules. Therefore, in the hydrogen-chlorine reaction water must play a part at some other stage.

The vapour tension of water necessary for the limiting value of the reaction velocity is not yet exactly known. According to the experimental results, the value lies between 10^{-5} and 4×10^{-6} mm. According to Chapman, the velocity results of Bodenstein and Dux in presence of moisture having a vapour pressure of less than 0.001 mm. seem doubtful. These experimenters have worked with a gas mixture containing oxygen. Moreover, Rideal and Norrish (*J. Chem. Soc.* **127**, 787 (1925)) have stated that hydrogen and oxygen combine in presence of chlorine, forming water in visible light. The success of the experiments of Coehn and his collaborators is due to the fact that there was no oxygen in their gas mixture. Hutton, in Chapman's laboratory, observed a very slow formation of HCl (about one molecule per quantum) with a specially dried gas mixture containing oxygen. It appears, therefore, that if water had any influence on the velocity of the reaction, one should have observed an acceleration during the course of the reaction.

It is interesting to note that the velocity of decomposition of hydrogen bromide or hydrogen iodide in presence of ultra-violet rays appears to be unaffected by moisture, whereas hydrogen chloride cannot be photochemically decomposed if thoroughly dried. The combination of chlorine and carbon monoxide is greatly reduced by desiccation, and the reaction between sulphur dioxide and chlorine appears to be completely stopped by protracted drying of the gas.

B. Lewis (*Nature*, **120**, 473 (1927)) has stated that the Nernst chain cannot be initiated in the absence of water vapour, but there is no evidence that water vapour functions in the chain itself. If water has a rôle in the chain mechanism, no chains should be propagated when a dry mixture of hydrogen and chlorine is exposed to radiation.

(9) These observations would lose much of their mystery if we could adopt the admittedly unproven hypothesis that the Nernst chains are initiated heterogeneously on the walls of the vessel. The minute traces of water necessary for the reaction are indeed such as would be just sufficient to form unimolecular layers on the surface of the vessel, and render this catalytically active. Similarly minute traces of nitrogen chloride, which can inhibit the combination, are just sufficient to act as catalytic poison by forming layers over the surface. There are very serious difficulties about supposing that only the light absorbed by a single layer of molecules, namely, those in contact with the surface of the vessel, is effective, as we must assume if the first part of this hypothesis is true. Weigert and Kellermann (*Z. physikal. Chem.* **107**, 1 (1923)) seem indeed to have shown directly that some of the chains are initiated in the body of the gas. On the other hand, if we assume that the water molecules actually take part in the chains, it is not easy to see why the reaction velocity should become independent of the pressure of water vapour at such small concentrations. It is necessary to suppose that the chlorine atoms have so long a life—Chapman estimates $1/50$ second—that every one is bound to meet a water molecule before it recombines. Only chlorine atoms which are actually attached to water molecules must be supposed to react.

For the purpose of following the rate of reaction, earlier investigators of the hydrogen-chlorine combination used exclusively an apparatus which contained, besides the gas mixture, a small amount of water. The volume decrease, resulting from solution in water of hydrochloric acid formed, was used as the indicator of the progress of reaction. Draper was the first to construct an apparatus of this type and to use it for systematic experiments. Draper, among other observations on the peculiarities of the hydrogen-chlorine reaction, described a particular initial effect of radiation, viz., that the volume or pressure decrease was always preceded by an initial increase of short duration. This so-called Draper effect was interpreted by later investigators as due to a heating of the gases by the absorbed light energy, and by the energy liberated in the reaction.

Induction period.—Bunsen and Roscoe in their experiments observed that the formation of HCl did not occur instantaneously on

illumination, but was preceded by a period of variable duration with almost no reaction taking place. This induction period, which for a long time was assigned an important rôle in the theoretical development of photochemistry, was found by Bunsen and Roscoe to be dependent not only on the mode of preparation of the gases but also on their former history, being, for instance, greatly shortened by a previous illumination. Chapman and co-workers (*J. Chem. Soc.* **89**, 1402 (1906); **97**, 845 (1909)) proved that the induction period is caused by the impurities in the gases used, as well as by impurities on the walls of the containing vessel and in the absorbing liquid. NH_3 , NCl_3 , ClO_2 , and some other compounds, it may especially be noted, increase the duration of the induction period enormously. All these substances are probably destroyed or eliminated from the gas phase on illumination, the full rate of HCl formation being attained only after this purification has taken place. The time necessary for the removal of impurities determines the period of induction. Chapman and MacMahon suggested for instance that NH_3 combined with HCl formed, and was in this way removed from the gas phase. Recently Norrish (*J. Chem. Soc.* **127**, 2317 (1925)) objected to this explanation, and suggested that a reaction takes place between illuminated Cl_2 and NH_3 , this reaction being localized on the illuminated walls of the containing vessel. Norrish pointed out that the rate of HCl formation is dependent on the H_2 concentration, and if the view of Chapman and MacMahon were correct, the duration of induction period caused by NH_3 should also be dependent on it. These authors observed, however, that the induction period was not affected by variations in the hydrogen concentration, which indicates, according to Norrish, that their theory is not correct. From theoretical considerations on the mechanism of the $\text{Cl}_2\text{-NH}_3$ reaction, Norrish obtained the following equation for the duration of the induction period:

$$T = K_1 [\text{NH}_3] \left[1 - \frac{K_2}{[\text{Cl}_2]} \right] \frac{V}{S}.$$

The square brackets indicate the corresponding concentrations, and V and S are respectively volume and illuminated surface of the vessel. The experimental results agreed fairly well with this equation, but the influence of surface was studied qualitatively, and hence the results appear to be unconvincing.

Baly and Barker (*J. Chem. Soc.* **119**, 653 (1921)) came to different conclusions concerning the nature of the induction period, and suggested that it is an inherent property of the hydrogen-chlorine reaction.

Consequently, the authors developed a theory of the reaction based partly on this conclusion. As Weigert (*Z. physik. Chem.* **106**, 428 (1923)) pointed out, the results of Baly and Barker's experiments are probably due to small traces of impurities, and cannot be convincing.

The duration of the induction period is not markedly modified by the presence of oxidizing agents, such as HNO_3 , HNO_2 , H_2O_2 , KMnO_4 , but small quantities of ammonia considerably increase the induction period, which can be suppressed by avoiding ammonia altogether. Nitrogenous organic matter, and NCl_3 , act as ammonia. It is sufficient that the gaseous mixture should contain a molecule of NCl_3 per 1,000,000 molecules of chlorine and hydrogen, in order to reduce the light sensitivity to $1/100$ of its normal value. It should be remarked that in the experiments performed in the laboratories of Bodenstein, Chapman, and Coehn with very pure gas, and avoiding all traces of ammonia, the phenomenon of induction was not observed.

The influence of oxygen. — Bunsen and Roscoe, Pringsheim (*Wied. Ann.* **32**, 384 (1887)) and Mellor (*J. Chem. Soc.* **81**, 1293 (1903)), studied the influence of oxygen in this reaction. Chapman and co-workers showed that the duration of the induction period was independent of the oxygen content, this latter uniformly retarding the rate of reaction. The fundamentally different nature of the action of oxygen, as opposed to those substances causing induction, was further demonstrated by Bodenstein and Dux. Their conclusion was that the retarding action of oxygen is proportional to its concentration (in agreement with the results of Chapman), and that its active concentration remains apparently constant throughout the course of reaction.

Kinetics of the process. — Bodenstein and Dux used a method which is distinct from that of the previous investigators, avoiding water as absorbing agent, but freezing out both Cl_2 and HCl by means of liquid air. From the residual pressure of H_2 and O_2 , the progress of the reaction was easily calculated. This method, possessing important advantages over the method usually employed before, enabled Bodenstein and Dux to study the rate of reaction at varying concentrations of the components, and to follow its whole course and not merely the initial stages.

The kinetics of this reaction seem highly complicated. Different workers have different equations.

The equation of Mrs. Chapman, already quoted, indicates that the rate of reaction is proportional to a varying power of the chlorine concentration slightly smaller than the second, is proportional to the hydrogen concentration provided it is small, but is slightly retarded

by hydrogen if present in excess. This last result is a confirmation of an early observation by Chapman and Underhill (*J. Chem. Soc.* **103**, 496 (1913)) which was criticized by Bodenstein. The term expressing the joint action of hydrogen and oxygen is important. This term takes account of Mrs. Chapman's observations that, with but little hydrogen present, the rate of reaction becomes almost independent of the oxygen concentration. Mrs. Chapman further found the rate of reaction to be independent of the total pressure in stoichiometric gas mixtures. N. Thon (*Z. physik. Chem.* **124**, 327 (1926)) now questions Mrs. Chapman's result that excess of hydrogen has a slight retarding effect; in a critical survey of the whole problem, Thon ("Die Chlor-knallgasreaktion", *Fortschritte der Chemie, Physik und physikalischen Chemie*, Band 18, Heft 11. Berlin (1926)) suggests the general formula:

$$\frac{dx}{dt} = \frac{K[\text{Cl}_2]^2[\text{H}_2]}{K'[\text{H}_2][\text{O}_2] + K''[\text{Cl}_2]}$$

and shows that, on the whole, the apparently divergent results of different investigators can be regarded as special cases of this general equation. With regard to the inhibition by oxygen, Thon calculates that the amount of water formed under ordinary conditions is negligible in comparison with the hydrogen chloride produced.

Quantum yield.—The synthesis of HCl is the most photo-sensitive reaction known. By changing the experimental conditions, Marshall (*J. Phys. Chem.* **29**, 1453 (1925)) has observed a quantum yield of 20,000 to 25,000 molecules. Miss Kornfeld and Müller's value is 25,000, with a mixture of hydrogen and chlorine in equal proportions, and under atmospheric pressure ($\lambda = 4360 \text{ \AA}$); under certain conditions the quantum yield goes up to 100,000. Recently Harries (*Proc. Nat. Acad. Sci.* **14**, 110 (1928)) has shown that in absence of oxygen and in blue light, the quantum yield is 6×10^5 molecules of hydrogen chloride per quantum. This value has not been surpassed experimentally.

Bodenstein (*Z. physik. Chem.* **85**, 329 (1913)), by comparing the light energy absorbed by Cl_2 in his experiments with the amount of HCl formed, came to the conclusion that as many as 10^6 molecules of Cl_2 reacted per absorbed quantum. This estimate is higher than the value obtained by Miss Kornfeld and Müller (*ibid.* **117**, 242 (1925)), who worked with highly purified gases almost free from O_2 . Their value is 10^5 molecules of HCl formed per quantum of light absorbed. The recent work of Porter, Bardwell, and Lind (*J. Amer. Chem. Soc.* **48**, 2603 (1926)) indicates reaction yields in excess of this figure. The main fact that

there is an enormous deviation from the Einstein law of photochemical equivalence cannot be doubted.

The work of Weigert and Kellermann is looked upon as direct evidence of some sort of chain mechanism, though it is never clear how an increased absorption of light can be associated with the formation of a chain. Using an intense spark of very short duration as the source of light, they demonstrated that the reaction did not proceed instantaneously, but required a measurable time for completion. This effect has, however, very little in common with the induction period already discussed, as the time is of a quite different order of magnitude, and this effect is longer in more sensitive and pure gas mixtures. From the observed period of about 0.01 second, and a calculated quantum yield of 10^6 , Weigert concluded, on the assumption of a chain reaction, that an atomic process required only 10^{-7} second for completion. Specially with respect to this observation of Weigert is it interesting to note that Bodenstein and Taylor (*Z. Elektrochem.* **22**, 202 (1916)), and more recently Marshall (*J. Phys. Chem.* **30**, 751 (1926)), failed to observe even the slightest reaction when previously illuminated Cl_2 was led into H_2 . The time interval between illumination and admixture in the experiment of Marshall did not exceed 3×10^{-4} second, oxygen free chlorine, with and without water vapour, being used.

Horiba and Ichikawa (*Sexagint Osaka Celebration*, Kyoto, **73** (1927)), have investigated the primary changes during the photochemical reaction between chlorine and hydrogen by recording the minute pressure changes of the reacting system on a photographic film, with the aid of an optical lever and oscillograph. No induction period was observed, but for an initial period of 1.5—2 sec. the velocity of the reaction changes with time, finally attaining a steady value, and it is this phase of the reaction which is more correctly termed the induction period. The authors support the theory of a chain mechanism.

Effect of pressure on quantum yield. — Recently Marshall (*J. Phys. Chem.* **29**, 1453 (1925)) has shown that at low pressures the quantum yield decreases very rapidly, being about 2×10^4 molecules per quantum at 60 mm. pressure and only 20 molecules at 0.101 mm. total pressure. Though the results are approximate, the main fact of a thousand fold decrease is fully established.

Effect of light intensity. — There is considerable difference of opinion amongst different workers regarding the relation between the intensity of the incident radiation and the velocity of the photochemical combination between hydrogen and chlorine. Draper (*Phil. Mag.* **23**, 401 (1843)), Bunsen and Roscoe (*Phil. Trans.* **146**,

355, 601 (1857)), Mrs. Chapman (*J. Chem. Soc.* **125**, 1521 (1924)), Miss Kornfeld and Müller (*Z. physik. Chem.* **117**, 242 (1926)), observed that the reaction between chlorine and hydrogen is directly proportional to the intensity of the incident radiation. Recently Allmand and Beesley (*Nature* **123**, 164 (1929)) obtained results similar to those of Mrs. Chapman, whilst Baly and Barker (*J. Chem. Soc.* **119**, 653 (1921)) showed that the velocity increases more rapidly than the intensity. All these workers used total light from electric bulbs. Recently, Marshall (*J. Phys. Chem.* **29**, 1453 (1925)) has investigated the same problem in presence of mercury arc light. The following results have been obtained by Marshall:

Distance from lamp in cms.	39	190	62.5
Molecules of HCl formed per hour $\times 10^{-21}$	35	13	26.0
Ratio of velocities	2.7	2	1.3
If directly proportional	25	9	2.56
If proportional to square root	5	3	1.6

Marshall's results show that the combination of chlorine and hydrogen in presence of mercury lamp radiation, which is more intense and active than the light used by previous workers, is proportional to less than the square root of the incident radiation.

Draper, Baly and Barker, and Mrs. Chapman used electrolytic gas, which always contains small amounts of oxygen. Miss Kornfeld and Müller removed oxygen from the hydrogen, but the chlorine they used may have contained a little oxygen. On considering the details of the experiments of Mrs. Chapman, and those of Baly and Barker, we are of the opinion that there was more oxygen present in Baly and Barker's experiments than in Mrs. Chapman's gas, and this will be evident from the following lines from Baly and Barker's paper: "During the course of this work we encountered considerable difficulty owing to the presence of oxygen in the reaction vessel."

Moreover the light intensity in the experiment of Mrs. Chapman was greater than in the case of Baly and Barker. It is well known that oxygen markedly retards the photochemical combination of hydrogen and chlorine; hence it appears that the photochemical reaction velocity in the experiments of Baly and Barker was not as much accelerated as that in the case of Mrs. Chapman's experiments. We have already emphasized that the greater the acceleration of the reaction by the absorption of incident light, the less is the chance of observing a direct or a square relationship between intensity and velocity. Consequently Baly and Barker observed a tenfold increase in velocity by increasing the light sixfold, whilst Mrs. Chapman working with a purer

reacting system containing less oxygen, and under more intense light than that used by Baly and Barker, observed about a 5.5 fold increase of velocity on a sixfold increase of light intensity. The results of Miss Kornfeld and Müller are on the same lines as those obtained by Mrs. Chapman. Marshall, working with very pure reacting substances, and with intense light from a mercury lamp, obtained a relation which is less than square root for the same chemical change. Hence the photochemical combination of chlorine and hydrogen can show a relationship lower than square root, direct, or nearly square, depending on the acceleration of the reaction caused by light.

Limit of wavelength. — Seebeck (*Goethe's Farbenlehre* 1810), and Silbermann (*Ann. chim. et phys.* **37**, 497 (1853)), have stated that red rays are without action, and blue and violet rays are active upon a moist mixture of hydrogen and chlorine.

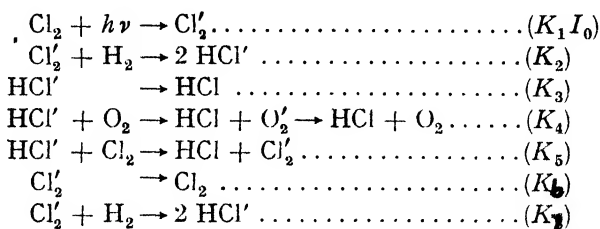
W. Taylor (*Phil. Mag.* **49**, 1165 (1925)) claims that no reaction could be obtained with light of wavelengths greater than 4900 Å, whilst Coehn and Jung (loc. cit.) calculate the limit of measurable reaction up to 5400 Å (equivalent to 52,500 cal.), and Weigert sets the limit at 5900 Å (*Z. physik. Chem.* **120**, 215 (1926)).

The active frequencies appear not to be confined to any restricted region, since, when light is filtered through chlorine, its photochemical activity falls rapidly not towards zero, but towards a definite residual value. Thus some of the very feebly absorbed frequencies must be active (W. Taylor *Trans. Faraday Soc.* **23**, 31 (1927); W. Taylor and A. Elliot *ibid.* **38**, 583).

According to the observations of Coehn and Jung, a dry mixture of chlorine and hydrogen is not sensitive to any radiation up to 3000 Å, but radiations of wavelength shorter than 2540 Å are active.

Theories of reaction. — Following his experimental study with Dux, Bodenstein developed a theory of the process, suggesting that chlorine molecules were ionized by absorption of light, and that the expelled electrons caused a chain reaction. Failure to detect ionization in illuminated chlorine (Thomson, *Proc. Camb. Phil. Soc.* **11**, 210 (1901), Kummell, *Z. Elektrochem.* **17**, 490 (1911), and Le Blanc and Volmer, *Z. Elektrochem.* **20**, 494 (1914)), led Bodenstein to propose a reaction mechanism involving activated molecules (*Z. Elektrochem.* **22**, 53 (1916)). Bodenstein suggested that activation consisted, not in high kinetic energy of the molecules, but in a change of electronic orbits, an idea later generalized and applied by Stern and Volmer to all photochemical reactions. He suggested, as the sequence of reactions occur-

ing in illuminated hydrogen-chlorine mixture, the following scheme (the activated molecules being here denoted thus: Cl_2'):

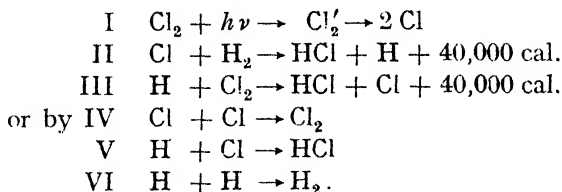


The activated molecules then repeat the cycle. The kinetic interpretation of these reactions gives the following equations:

$$\begin{aligned} + \frac{d[\text{HCl}']}{dt} &= I_0 K_1 K_2 [\text{Cl}_2] + K_7 [\text{Cl}_2'] [\text{H}_2] \\ - \frac{d[\text{HCl}']}{dt} &= K_3 [\text{HCl}'] + K_4 [\text{HCl}'] [\text{O}_2] + K_5 [\text{HCl}'] [\text{Cl}_2] \\ + \frac{d[\text{Cl}_2']}{dt} &= K_5 [\text{HCl}'] [\text{Cl}_2] \\ - \frac{d[\text{Cl}_2']}{dt} &= K_6 [\text{Cl}_2'] + K_7 [\text{Cl}_2'] [\text{H}_2]. \end{aligned}$$

In order to eliminate the concentrations of hypothetical activated molecules from this set of equations, Bodenstein assumed that, almost immediately on illumination, a stationary state is reached in the gas mixture in which the concentrations of the active molecules remain constant, the differential quotients on the left of the two pairs of equations thus becoming equal to each other.

Nernst chain mechanism.—Nernst (*Z. Elektrochem.* **24**, 355 (1918)) suggested that the primary action of light consisted in a dissociation of chlorine into atoms, these reacting by the sequence:



The reactions II and III, in which there is alternate formation and disappearance of atomic hydrogen and chlorine, will recur a large number of times, and thus the large quantum yield is explained.

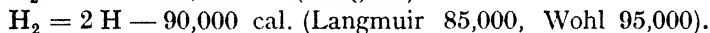
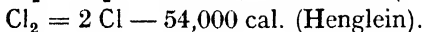
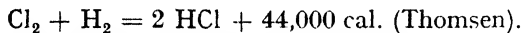
The heat of dissociation of chlorine is still very unsatisfactorily known. Pier and Russel's value (100,000 cal.) is too high. The value of Wartenberg (*Z. Physik* **26**, 54 (1920)) is 70,000 cal., and the values of Trautz (*Z. anorg. Chem.* **102**, 122 (1918); *Z. Physik* **21**, 605 (1920)), carried out by two methods, are 70,000 and 61,000 cal. The careful measurements of Henglein (*Z. anorg. Chem.* **123**, 137 (1924)) give the value 54,000, which is probably the most correct.

If one admits that the quantum of active light should be at least equal to the heat necessary for dissociating a molecule of chlorine, the limit of active wavelength can be calculated from the relation

$$E = N h \nu = \frac{28,500}{\lambda_{\mu}}, \text{ in which } E = \text{heat of dissociation of chlorine.}$$

One finds that a mixture of chlorine and hydrogen ought to be sensitive to radiations of wavelength 5300 Å.

The thermal results of reactions II and III have been calculated according to the following data:



According to these results, reactions II and III give out heat and thus are considered to be probable.

The reaction II is only feebly exothermic, and as the heat measurements are not very accurate, the reaction may be endothermic, and hence Coehn argued that reaction II does not occur in the formation of HCl.

Though the theory of Nernst is not contradicted by thermochemical data, it is not supported by kinetic measurements.

(1) If the reactions V and VI are negligible in comparison with IV, then the velocity is given by the relation

$$\frac{d[\text{HCl}]}{dt} = K I_0^{\frac{1}{2}} [\text{Cl}]^{\frac{1}{2}} [\text{H}_2].$$

(2) If the reactions IV and V are negligible in comparison with VI, then the velocity is

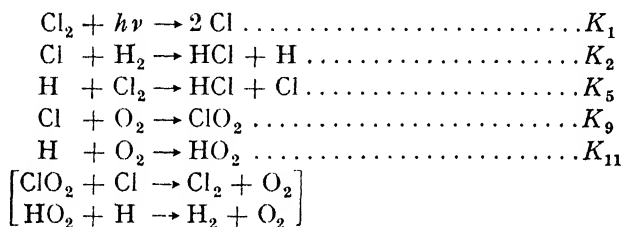
$$\frac{d[\text{HCl}]}{dt} = K I_0^{\frac{1}{2}} [\text{Cl}_2]^{\frac{3}{2}}.$$

(3) If the reaction IV and VI are negligible in comparison with V, the velocity becomes

$$\frac{d[\text{HCl}]}{dt} = K I_0^{\frac{1}{2}} [\text{Cl}_2] [\text{H}_2]^{\frac{1}{2}}.$$

One can at once see that none of these velocity equations is in agreement with the observed facts. In particular, they are always contrary to the observation regarding the influence of intensity, in which a proportionality relation has been actually observed by some workers, but Nernst's relation gives a square-root relationship. Moreover, Nernst's conception does not take into consideration the influence of water vapour, which plays an important part.

Göhring's mechanism.—Later, Göhring (*Z. Elektrochem.* **27**, 511 (1921)) showed that Nernst's mechanism could lead to a kinetic equation representing Bodenstein's experimental results. Assuming a sequence of reactions:

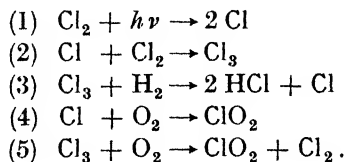


Göhring derived the following equation:

$$\frac{d[\text{HCl}]}{dt} = 2 K_1 I_0 \frac{2 K_2 K_5 [\text{Cl}_2]^2 [\text{H}_2] + K_2 K_9 [\text{Cl}_2] [\text{H}_2] [\text{O}_2]}{[\text{O}_2] K_2 K_{11} [\text{H}_2] + K_5 K_9 [\text{Cl}_2] + K_9 K_{11} [\text{O}_2]^2}.$$

Neglecting the second term in the denominator on account of the low concentration of oxygen, and assuming $K_2 = K_5$, $K_9 < K_{11}$, this equation is reduced to a form, in which it is in accord, not only with the experiments of Bodenstein and Dux, but also with the recent experiments of Thon.

Thon points out that the same formula is derived if, instead of free chlorine atoms, trichlorine molecules, Cl_3 , be assumed as the reacting species. The sequence of reactions is then represented by the scheme:



Thon suggests that this second scheme is less objectionable than that of Göhring. The suggested atomic chain mechanism seemed to be in disagreement with the observed non-reactivity of Cl_2 a very short

time after illumination. Warburg (*Z. Elektrochem.* **27**, 139 (1921)) calculated on the basis of the original Nernst scheme the mean life of chlorine atoms, and came to the conclusion that if these were formed, Bodenstein and Taylor should have observed a rapid rate of reaction on mixing illuminated chlorine and hydrogen. Göhring, however, using his own reaction scheme, which includes the reaction of chlorine atoms with oxygen, calculated that in the experiments of Bodenstein and Taylor no measurable reaction could take place. Göhring's explanation is not valid for Marshall's experiments, where oxygen-free chlorine was used. Marshall, therefore, suggests that chlorine atoms are cleaned up and recombined to form molecules, on the walls of the narrow capillary connecting the illuminated chlorine with the hydrogen container.

Chapman's views are based on the assumption of active molecules. It was suggested that, in the illuminated gases, an equilibrium $\text{Cl}_2' + \text{O}_2 \rightleftharpoons \text{Cl}_2 + \text{O}_2'$ is established, activated oxygen then occasionally combining with hydrogen to form water. The derived equation is

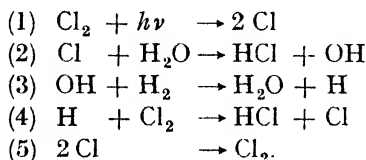
$$\frac{d[\text{HCl}]}{dt} = \frac{K_1 [\text{Cl}_2] [\text{H}_2]}{K_2 [\text{H}_2]^2 [\text{O}_2] [\text{Cl}_2]'}$$

and it is supposed also to account for the high quantum yield of the reaction, if the assumption be made that the active HCl molecules formed transmit their energy only to chlorine. Baly and Barker (*J. Chem. Soc.* **119**, 653 (1921)), assuming a mechanism very similar to that of Bodenstein, suggest, however, that the transmission of the activation energy goes *via* re-emission and re-absorption of light, deducing from this assumption their observed lack of proportionality between the reaction velocity and light intensity. This last deduction seems incorrect, and it can be easily shown that their theory leads to direct proportionality of light intensity and reaction velocity.

Coehn's views. — According to the experiments of Coehn and Jung, the quantum necessary for starting the reaction is not the same in the dry and the moist gases. It appears, therefore, that the processes are not the same in both cases. Coehn and Jung have observed that the smallest quantum necessary for the reaction with moist gas mixture corresponds to $\lambda = 5400 \text{ \AA}$, and is practically equal to the heat of dissociation of a molecule of chlorine; whilst the quantum for the dry mixture corresponding to $\lambda = 2540 \text{ \AA}$ is sufficient to dissociate a molecule of hydrogen (Wohl's value = 95,000 cal.). Thus $E = N h \nu = \frac{28,500}{0.254} = 112,000 \text{ cal.}$ Coehn and Jung have thus come to the conclusion that visible light

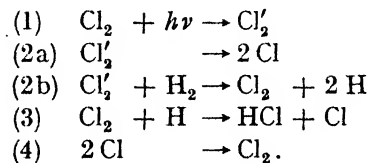
dissociates molecules of chlorine, but that the free atoms thus formed are not capable of reaction with hydrogen. In the absence of moisture, they recombine and do not form HCl; in the moist gas they react with water and form a chain of reaction, like that imagined by Nernst.

The mechanism can be represented by the following scheme:



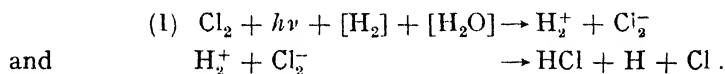
In support of their views Coehn and Jung state that, thermodynamically, the direct reaction of a chlorine atom with a hydrogen molecule is rather improbable, if the recent thermochemical data on the heats of dissociation ($\text{Cl}_2 \rightarrow 2 \text{Cl} = 54,000 \text{ cal}$; $\text{H}_2 \rightarrow 2 \text{H} = 95,000 \text{ cal}$.) be used. Further, the smallest energy quantum capable of causing the reaction in dry gas must be equal to the heat of dissociation of the hydrogen molecule, and actually Coehn and Jung calculate from the wavelength 3000 \AA , $94,500 \text{ cal}$. as the lowest limit for it.

The quantum of ultra-violet light necessary for the dry gas mixture acts in another fashion. The molecule of chlorine which absorbs the quantum can transmit its energy to the hydrogen molecule in the same way as in the experiments of Cario and Franck with mercury vapour. The molecule of hydrogen gets dissociated into free atoms, which combine with chlorine. In the dry gas mixture the following processes are supposed to take place:

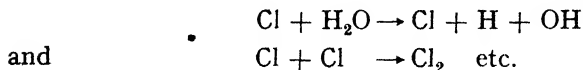


The quantum yield, in absence of moisture, cannot exceed 2 molecules of HCl per quantum absorbed; its exact value has not yet been determined. The experiments of Coehn and Heymer. (*Naturwiss.* **14**, 299 (1926)) show that the yield per quantum does not exceed seven molecules. Whatever it may be, it appears from the observations of Coehn that water vapour not only plays an important part in the beginning of the reaction but also is necessary in the chain of secondary reactions. Several objections have been raised to the

views of Coehn. Weigert (*Z. physik. Chem.* **106**, 426 (1923)) objects to Coehn's chain mechanism for the moist gases, since it involves water molecules in the chain mechanism, and therefore in the expression for the reaction velocity. The data of Bodenstein and Dux regarding the absence of the influence of water between wide limits contradict the views of Coehn. Weigert therefore suggests that the water molecules are a component part of the primary photochemical system, a cluster of hydrogen and chlorine molecules. The action of water is to facilitate an inner photoelectric effect between hydrogen and chlorine. His idea can be symbolized by the following scheme:



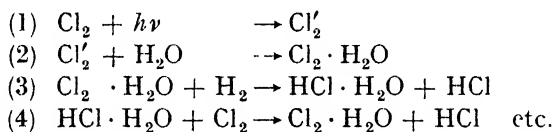
Cathala (*Compt. rend.* **181**, 33 (1925)) makes a similar objection to Coehn's theory, and develops a chain mechanism in which water does not take part in the chemical reactions, but in virtue of its dipole nature and high electric moment facilitates certain reactions of other components. Because of their dipole nature, the water molecules exert an action which activates the neighbouring molecules. The only effective encounters are the very ones which are within the sphere of action of water molecules. Norrish has remarked, however, that in order to explain the influence of small quantities of water, it is necessary to attribute to its sphere of action very large dimensions, which should be 500 times larger than that of the "sphere of collision". It is interesting to note that a molecule of HCl having greater electric moment than one of water has no catalytic activity. Finally, the processes imagined by Cathala, and according to which there will be an intermediate formation of molecules of ClO_2 and Cl_3 , do not seem to be true, because then the velocity of the reaction would have been proportional to $I^{\frac{3}{2}}$, which seems contrary to the most accurate experimental measurements. The objection of Weigert to Coehn's theory is not fully justified. In fact the influence of water on the reaction velocity will be determined by the relative speeds of the reactions



Thus it will be represented by an equation of the type

$$\frac{K_1[\text{H}_2\text{O}][\text{Cl}]}{K_2[\text{Cl}]^2 + K_1[\text{H}_2\text{O}][\text{Cl}]}$$

which shows that from a certain concentration upwards the influence of moisture is negligible. Making use of similar considerations, Cathala calculated the rates of the two competitive reactions of chlorine atoms, concluding, as was mentioned before, that Coehn's mechanism is unsatisfactory. This calculation of Cathala is by no means conclusive, since he arbitrarily assumes that the reaction of two chlorine atoms is successful on every collision. Coehn's theory is, however, not free from various other objections, as for instance, it does not explain the action of oxygen, and in its present form leads to a reaction velocity equation in which the square root of the light intensity is involved. Chapman (*Trans. Farad. Soc.* **21**, 547 (1925)) suggests, therefore, that activated chlorine molecules are primarily formed, and react with water to form molecular compounds which initiate a chain of reactions alternately with hydrogen and chlorine molecules, HCl being ultimately formed. Chapman's scheme is as follows:



We may now indicate here that the general expression obtained by Mr. and Mrs. Chapman,

$$\frac{d[\text{HCl}]}{dt} = \frac{K_1 I_0 [\text{Cl}_2]^2 [\text{H}_2]}{K_2 [\text{H}_2]^2 [\text{O}_2] + [\text{Cl}_2]},$$

does not exactly correspond to that established empirically. It has to be remarked that if the velocity of the reaction is really independent of the tension of water vapour when it exceeds 10^{-5} mm., it follows according to the hypothesis of Chapman that the life period of active chlorine molecules should be at least 0.01 sec.

Both Cathala and Norrish have stated that the hypothesis of Coehn and Jung implicates a very feeble tendency of the chlorine atoms to combine amongst themselves. The life period of these atoms should attain at least 10 seconds, which is incompatible with the limiting value ($1/1600$ second) found by Bodenstein. Moreover, all theories according to which the velocity of the disappearance of the active substance (Cl) is proportional to the square of its concentration, imply a velocity of formation of HCl proportional to the square root of the light intensity. In this respect, the theory of Coehn and Jung is subject to the same criticism as that of Nernst.

The view has been given out by Norrish (*Z. physik. Chem.* **120**, 205 (1926)) that water in the gaseous state does not exert any influence on the reaction, but that water condensed on the wall of the vessel is the active substance. This opinion is founded essentially on the fact that, in the experiments of Coehn and Jung, the quantity of water vapour introduced into the apparatus, which corresponds to a pressure of 10^{-5} mm, is just sufficient for forming a layer one molecule thick on the walls of the vessel. The primary photochemical phenomenon will take place uniquely in contact with this layer, and will attain its maximum when the layer completely covers up the surface of the vessels. According to Bodenstein this view is inadmissible, because the velocity of the reaction is proportional to the quantity of light absorbed by the gas mixture, and not to the illuminated surface. Also Weigert has remarked that the hypothesis of Norrish is against the fact observed by Weigert and Kellermann, that the formation of HCl takes place on the passage of the luminous rays. Recently, Coehn and Heymer (*Ber.* **59**, 1714 (1926)) have confirmed the view that hydrogen and chlorine unite without the intervention of the glass surface.

The influence of oxygen on this reaction has not the same importance as that of water vapour. This constitutes an accessory phenomenon, which it is possible to avoid by working with pure chlorine. A different supposition has been made regarding the mode of action of oxygen.

Generally, the amount of oxygen has been assumed to be constant to the end of the reaction. However, Weigert (*Ann. Physik* **24**, 55, 243 (1907)) observed the formation of water in a mixture of chlorine, hydrogen, and oxygen, illuminated by visible light. Certain authors, notably Cathala and Göhring (*Z. Elektrochem.* **27**, 511 (1921)), have assumed a chemical action of active chlorine with oxygen, and the formation of compounds like ClO_2 and H_2O_2 (Göhring). The experiments of Mrs. Chapman have shown that the influence of oxygen manifests itself solely when the pressure of hydrogen is very feeble, and increases up to a limiting value with this pressure. Mr. and Mrs. Chapman have tried to account for these facts on the assumption that the molecules of chlorine can be deactivated by giving up their energy to oxygen, and the reaction appears reversible. The molecules of oxygen thus activated can give up their energy to chlorine, or enter into reaction with hydrogen forming water. The anticatalytic action of oxygen is thus connected with the phenomenon of sensitization, which is a counterpart of this anticatalytic action.

Recently Norrish and Rideal (*J. Chem. Soc.* **127**, 789 (1927)) studied the kinetics of the process, and found that the rate of

formation of water could be expressed by the equation

$$\frac{d[\text{H}_2\text{O}]}{dt} = K[\text{Cl}_2][\text{O}_2],$$

hydrogen concentration apparently not influencing the velocity of reaction. The authors did not study the simultaneous formation of HCl; but from the data contained in their paper one can estimate that the rate of formation of HCl, even in these oxygen-rich mixtures, is about 5–10 times more rapid than the formation of water. The theory of Norrish and Rideal implies the formation of activated chlorine molecules by the absorption of energy, and the subsequent activation of oxygen by collisions with chlorine, this activated oxygen further reacting with hydrogen to form water. Norrish and Rideal suggest, also, that the retarding effect of oxygen on HCl-formation has nothing in common with the observed formation of water, this being a primary reaction. This proposed double action of oxygen seems to be an unnecessary complication. An estimation of the amount of water which could be formed, for instance, in Bodenstein's experiments, shows that only a small portion of oxygen would be used up in this process, its active mass thus remaining approximately constant, as was assumed by Bodenstein. The question whether water formation is actually a primary reaction, and not one induced by the chains forming hydrogen chloride, cannot be answered at the present time. Tramm succeeded in preparing dry gases, which were not absolutely oxygen free, but nevertheless did not react even on prolonged illumination by visible light. On the other hand, Chapman states (*Trans. Faraday Soc.* **21**, 547 (1925)) that in his laboratory Hutton was unable to prepare dry oxygen-containing gases which were completely insensitive to visible radiation. This last result, further confirmed, will be a direct evidence that water formation is a primary photosensitized reaction, independent of HCl formation, as was assumed by Norrish and Rideal.

Miss Cremer (*Z. physik. Chem.* **123**, 285 (1927)) has recently extended work to higher oxygen concentration than in Bodenstein and Dux's investigation on the formation of hydrochloric acid from its elements, in light, in presence of oxygen. It is calculated that when oxygen concentration is zero, the maximum yield of hydrogen chloride per quantum is 7.6×10^6 molecules.

Recently Cathala (*J. Chim. phys.* **25**, 182 (1928)) has stated that since the threshold frequency for the photochemical reaction between hydrogen and chlorine is nearly equal to the frequency corresponding

with the beginning of continuous absorption in the absorption spectrum of chlorine, it may be affirmed that the first stage of the photochemical reactions of the halogen molecule is the dissociation into neutral atoms, this process taking place strictly in accordance with the Stark-Einstein law. Theories involving the formation of active molecules and exchanges of activation between molecules by impacts are therefore to be discarded. (Compare Bancroft and Morton, *Proc. Nat. Acad. Sci.* **15**, 438 (1929).)

Since the free atoms are formed in amounts which are proportional to the time, though their concentration remains extremely small, it is necessary to postulate the existence of some process whereby they are destroyed. The hypothesis is therefore advanced that Cl_3 molecules are formed by the reaction $\text{Cl} + \text{Cl}_2 = \text{Cl}_3$. These collide with free atoms, and at the moment of impact there is regrouping of electronic orbits, forming "quasimolecules" according to the equation $\text{Cl}_3 + \text{Cl} = 2 \text{Cl}_2$, which then pass out among the other molecules of the gas and there lose their surplus energy. A similar process occurs with both bromine and iodine.

Chapman and Grigg (*J. Chem. Soc.* 3233 (1928)) have shown that under the same conditions of illumination, the velocity of the photochemical reaction between chlorine and hydrogen in capillary tubes is considerably less than in wider tubes. This result has been explained by the hypothesis that the union of the gases is due to an unstable catalyst, which is formed by light, and is destroyed when it comes into contact with glass. Trifonov (*Z. physik. Chem. B*, **3**, 195 (1929)) has shown that at low pressures (about 10 mm.) the quantum yield in the photochemical reaction is proportional to the square of the diameter of the vessel. This is ascribed to the cessation of the chain reactions $\text{H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H}$, $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$, at the walls of the vessel, due to the adsorption of hydrogen and chlorine atoms. With increase of pressure, the formation of hydrochloric acid becomes independent of the dimensions of the vessel.

Rollefson (*J. Amer. Chem. Soc.* **51**, 770 (1929)) has studied the photosynthesis of hydrochloric acid at low pressures, with excess of chlorine, and the reaction has been found to follow the relation

$$\frac{d[\text{HCl}]}{dt} = KI_0[\text{H}_2][\text{Cl}_2].$$

It is concluded that the action of light on this reaction is to form chlorine atoms in the $2 P_1$ state, which serve as the starting point for the reaction chain.

Recently Trifonov (with Rjabinin) (*Z. physik. Chem. B*, **6**, 118 (1929)) has reported that above 0.2 mm. pressure, the velocity of this photochemical reaction is proportional to the cube of the pressure, in agreement with Semenov's calculations. Below this pressure, the reaction either ceases or proceeds very slowly.

In a recent communication Wulf (*Proc. Nat. Acad. Sci.* **16**, 27 (1930)) has calculated the temperature coefficients of the photosynthesis of hydrochloric acid, in radiations of different wavelengths, from the energies of vibration for the first six vibrational levels of the normal chlorine molecule. His results show that the temperature coefficients vary from 1.68 to 0.994, when the spectral regions vary from 5492 Å to 4659 Å.

It appears to the writer that these variations of the temperature coefficients are much greater than those actually observed by Padoa and Butironi (*Atti Accad. Lincei* **25**, II, 215 (1916)), and others.

Spectral evidence. — From theoretical considerations on the relations between the absorption spectra and molecular binding of diatomic molecules, Franck was led to the conclusion that a halogen molecule can be dissociated on absorption of light into an ordinary atom and a metastable one. Chlorine, as well as bromine and iodine, shows, on closer investigation, a complicated system of absorption bands in the red and yellow parts of the spectrum, converging to a limit from which a continuous absorption extends towards the ultra-violet (Mecke, *Ann. Physik* **71**, 104 (1924); Kuhn, *Z. Physik* **39**, 77 (1926)). The convergence limit in Franck's interpretation represents the longest wave still capable of dissociating a halogen molecule into atoms, a normal and an excited one.

Recently an exact spectroscopic determination of the energy levels of halogen atoms by Turner (*Physic. Rev.* **27**, 397 (1926)) permits us to calculate exactly the amount of energy which is used for excitation of one of the atoms by light absorption, resulting in the dissociation of the halogen molecules. As an illustration, a table from Kuhn's paper (*Naturwiss.* **14**, 600 (1926)) is reproduced below:

Halogen	Convergence limit	Heat of dissociation from thermo-chemical data	$Nh\nu_e$ in cal.	Heat of dissociation
Cl ₂	4785 Å	57.0 cal.	59.4	56.9 cal.
Br ₂	5107	46.2	55.6	45.2
I ₂	4995	34.5	56.8	35.2

In applying Franck's theory to the treatment of the hydrogen-chlorine reaction, we must remember that Franck's arguments were developed for the case of a dissociation not induced by molecular collisions on light absorption. Another process can be imagined for molecules which absorb energy quanta smaller than those of the convergence limit. If the mean life is of the usual order of magnitude (10^{-7} — 10^{-8} sec.), then at ordinary pressures the activated chlorine molecules will suffer many collisions before emission of light, and it is not certain that a molecule which has absorbed an energy quantum less than that of the convergence limit, but still comparable with the heat of dissociation into two normal atoms, cannot suffer this process of collision.

Comparing the two types of proposed chain reactions—those involving atoms and those with excited molecules—we note that to reach a definite decision at present is by no means easy. Undoubtedly, the recent measurements of Thon are in favour of the atomic chain theory; but the difficulties inherent in the kinetic measurements of a reaction which is so sensitive to impurities, convince us that the results of Thon are not decisive. Moreover, Thon's assumption that the active mass of oxygen remains constant is not correct, and hence his empirical equation has to be modified.

✓ Other means of comparing the two rival theories of the reaction mechanism are by comparison with such experimental facts as: (1) the direct proportionality of the reaction rate and light intensity; (2) the rapid decrease of the quantum yield at very low pressures; (3) the influence of water vapour, and the action of different wavelengths on dry and moist gases. The first point excludes all reaction schemes in which the recombination of the atoms to form initial molecules is assumed to be the cause of the limited length of a chain of reactions, as all such theories unavoidably yield a final equation in which the square root of the light intensity is involved. Taking a simple case, we assume that the rate of reaction is proportional to the concentration of chlorine atoms. The rate of their formation is in the simple form:

$$+ \frac{d[\text{Cl}]}{dt} = K_1 I_0 [\text{Cl}_2],$$

and the rate of disappearance:

$$- \frac{d[\text{Cl}]}{dt} = K_2 [\text{Cl}]^2$$

from which equations it follows that the rate of reaction is proportional to

$$[\text{Cl}] = \sqrt{\frac{K_1 I_0 [\text{Cl}_2]}{K_2}}.$$

If, on the other hand, we can assume that the rate of disappearance of the reacting atoms is unimolecular with respect to their concentrations, the above objection to the atomic chain mechanism is not valid (compare Göhring).

The decrease in quantum yield at low pressures was observed by Marshall (*J. Phys. Chem.* **29**, 1453 (1925)), and by Marshall and Taylor (*Ibid.* **29**, 842 (1925)), who observed, by admitting atomic hydrogen to a mixture of chlorine and hydrogen, that the yield of HCl per hydrogen atom increased rapidly at higher pressures. It would seem, therefore, that a mechanism in which activated molecules are involved, with their simultaneous deactivation by re-radiation, would give a more ready explanation of the facts. However, if we assume together with Marshall (*Trans. Am. Elektrochem. Soc.* **49**, 143 (1926)) that chlorine atoms, like those of hydrogen, are "cleaned up" and recombine on the glass walls of the vessel, a decrease of the yield must be observed at low pressures.

The evidence of Coehn and Jung's experiments, especially the different action of visible and ultra-violet light on dry gases, seems to support the view that chlorine atoms in the one case and probably hydrogen atoms in the other are the intermediate products of light action.

The absorption of light by chlorine between 2540 Å and 6430 Å has been determined by von Halban and Siedentopf (*Z. physik. Chem.* **103**, 71 (1922)) for 19 wavelengths, using lines of mercury, zinc, and cadmium arcs, and between 3830 Å and 4510 Å for 12 wavelengths, using a "Nitra" lamp and photoelectric cell. The results show that within the pressure limits 760 mm. and downwards, Beer's law is true. The absorption curve shows a maximum in the ultra-violet at 3340 Å, and a minimum in the yellow. From yellow to red the absorption again increases, and reaches a maximum between 6140 and 6430 Å. No difference could be observed between the absorption of dry and moist chlorine.

According to Ribaud (*Ann. Physik* **12**, 107 (1919)), and Kuhn (*Z. Physik* **39**, 77 (1926)), the maxima for the absorption by I_2 , Br_2 and Cl_2 lie 400, 900 and 1400 Å respectively, to the violet side of the critical wavelengths required for dissociation into a normal and

excited atom respectively. These critical wavelengths are 4995, 5107, and 4785 Å, and thus the three maxima lie at 4595, 4207 and 3385 Å respectively. The continuous absorption by I_2 , Br_2 and Cl_2 is due to molecules in the lowest vibrational state. In a recent communication Bodenstein (*J. Chem. Soc. Ind.* **49**, 139 (1930)) has stated that the view that chlorine atoms are formed on illumination of a chlorine molecule is supported to a certain extent by the analysis of the absorption spectrum of chlorine.

From a critical examination of the experimental results, it appears to the author that the relation between velocity and intensity of the photochemical combination between hydrogen and chlorine will vary from $\frac{1}{4}$ to $\frac{3}{2}$. If the reaction is illuminated by intense ultra-violet light, and is largely accelerated, the velocity is likely to be proportional to $I^{\frac{1}{4}}$ or $I^{\frac{1}{3}}$. On the other hand, when the reaction takes place in radiations which are not markedly absorbed by the mixture, and the reaction is only feebly accelerated, the velocity may be proportional to $I^{\frac{3}{2}}$. Moreover, the quantum yield is likely to vary considerably with intensity, and the following results of Marshall (*J. Phys. Chem.* **29**, 1453 (1925)) are in agreement with this view:

Distance from the lamp in cm.	Intensity of light porportional to	Apparent quantum yield	Quantum yield calculated on the basis of direct proportionality
39	0.0006574	20.6	—
62.5	0.0002560	2.5	7.8
119.5	0.00007002	1.9	2.18
190	0.00002770	2.0	0.824

(Compare Bhattacharya and Dhar, *J. Indian Chem. Soc.* **6**, 473, 523 (1929).)

Hence it is clear, from the above table, that the quantum yield in the photochemical reaction between chlorine and hydrogen decreases with the increase in the light intensity.

It has already been mentioned that, regarding the limit of wavelength capable of initiating the photochemical combination between hydrogen and chlorine, there is considerable difference of opinion. Weigert (*Z. physik. Chem.* **120**, 215 (1926)) has set the limit at 5900 Å. From researches which are in progress in the author's laboratory, it is evident that in presence of radiations of wavelengths 5750—5800 Å, 5760—6140 Å, 6659 Å, and 6390—7180 Å there is appreciable chemical reaction between chlorine and hydrogen. Even in presence of radiation

of wavelength 7304 Å, which is the limit of the red end of the visible spectrum, there appears to be a slow chemical reaction between hydrogen and chlorine at 32.5°. Blank experiments show that at this temperature there is no reaction in the dark.

Several years ago, H. Sirk (*Z. physik. Chem.* **61**, 545 (1908)) showed that chlorine and hydrogen combine in the dark when heated to the temperature of 258°; the temperature coefficient of the reaction in the dark has a value 1.6 between the temperature limits 258° to 268°. On applying the Perrin-Lewis radiation hypothesis, we can calculate the wavelength necessary for the activation of the reaction from the temperature coefficient, and it is found to be 10,714 Å. Sachtleben (*Diss. Hannover* (1914)) found that the temperature coefficient of the dark reaction between hydrogen and chlorine is 2.04 between the temperature limits 146.5° and 160.1°, and hence the limiting wavelength necessary for activation of the reaction comes to be 11,110 Å, a value which is of nearly the same order as that obtained from Sirk's data (compare Christiansen, *Z. physik. Chem. B* **2**, 405 (1929)).

Having investigated numerous reactions in infra-red radiations, the author ventures to state that the limiting wavelength for inducing the photochemical combination of hydrogen and chlorine is of the order of 10,000 Å, and any radiations shorter than this are likely to accelerate the reaction, but radiations longer than this wavelength would not accelerate the change (compare Bhattacharya and Dhar, *J. Indian Chem. Soc.* **6**, 451 (1929); *J. Chim. phys.* **26**, 556 (1929)).

It appears fairly certain that the atomization of a chlorine molecule is not possible in all photochemical reactions with these radiations, because the wavelength necessary to atomize a molecule of chlorine is 5400 Å. Our researches, as well as those of Weigert (*Z. physik. Chem.* **120**, 215 (1926)), show that radiations longer than 5400 Å are capable of starting the photochemical reaction between hydrogen and chlorine. In all these cases activated molecules of chlorine take part in the photochemical changes. Moreover, with numerous reactions involving halogens, wavelengths longer than the values necessary for atomization of the halogens have been found to be photochemically active. Hence the author is forced to the conclusion that in all the reactions involving halogens, atomization of a halogen molecule is not always a necessity, and the photochemical reaction can be brought about by the formation of active molecules of the halogens by absorption of radiations longer than those necessary for atomization of a halogen molecule (vide Schultz, *J. Chim. phys.* **26**, 475 (1929)).

By comparing the velocity of the photochemical combination of chlorine and hydrogen in a capillary tube with that in a wider one, Chapman and Grigg (*J. Chem. Soc.* 2426 (1929)) have deduced the life period of the "catalyst" formed by the action of light. The calculated life period is approximately proportional to the light sensitivity of the mixture of chlorine and hydrogen.

Hence it is clear that the photochemical combination of hydrogen and chlorine is very complicated, the mechanism is far from being clear, and the reaction is highly susceptible to traces of impurities.

FORMATION OF CARBONYL CHLORIDE.

This reaction is similar in many respects to the photochemical combination of hydrogen and chlorine.

Wildermann's experiments (*Phil. Trans.* 199 A, 337 (1902); *Z. physik. Chem.* 42, 257 (1903)) with dry and purified mixtures of chlorine and carbon monoxide, indicate that the rate of reaction can be expressed by the kinetic equation:

$$\frac{d[\text{COCl}_2]}{dt} = KI_0[\text{Cl}_2][\text{CO}].$$

The reaction mechanism is complicated by the fact that oxygen exerts a retarding influence on this reaction. Chapman and Gee (*J. Chem. Soc.* 99, 1726 (1911)) showed that the velocity of phosgene formation is inversely proportional to the oxygen concentration only when this latter is small, these authors being able to represent their observations by the formula:

$$\text{Reaction velocity} = A + \frac{B}{[\text{O}_2]}.$$

Chapman and Gee reported that the period of induction observed in this reaction by earlier investigators (Dyson and Harden, *J. Chem. Soc.* 83, 201 (1903)) is due, just as in the reaction of chlorine with hydrogen, to the presence of impurities, nitric oxide, ozone, and nitrogen chloride being found very active in this respect. Moreover, Chapman and Gee observed that at higher temperatures (nearing 350°), the rate of photochemical reaction is much slower than at room temperature.

Bodenstein and co-workers (*Rec. trav. chim. Pays-Bas* 41, 585 (1922)); *Sitzb. Preuss. Akad.* 13, 104 (1926)) expressed the kinetics of

phosgene formation with moist gases at about 18° by the following equation:

$$+ \frac{d[\text{COCl}_2]}{dt} = K \sqrt{I_{\text{abs}}[\text{CO}]} [\text{Cl}_2],$$

the temperature coefficient between 18° and 28° being unity. Water vapour between the limits 0.02 and 15 mm. has very little influence on the velocity of the reaction. Since the reaction velocity is proportional to the square root of the absorbed light energy, the quantum yield must be dependent on the intensity of the light source used. The determination of the quantum yield loses therefore much of its significance. Under Bodenstein's experimental conditions, as many as 1000 phosgene molecules were formed per absorbed quantum. Hence the reaction is supposed to have chain mechanism. We have already stated that intensive drying greatly retards the photochemical combination between hydrogen and chlorine. The influence of drying is less pronounced on the velocity of phosgene formation, and according to Bodenstein drying decreases the velocity to $1/10$ — $1/100$ of the original velocity, and the reaction velocity with the dry gases is expressed by the following relation

$$\frac{d[\text{COCl}_2]}{dt} = K I_{\text{abs}} [\text{Cl}_2] [\text{CO}].$$

The raising of the temperature by 200—300 degrees also markedly decreases the velocity. Oxygen under these conditions loses its retarding action almost entirely. Weigert (*Ann. Physik.* **24**, 55 (1907)) stated that at temperatures nearing 500° the thermal equilibrium of phosgene and its decomposition products is not appreciably changed by illumination, although the velocity of its attainment is considerably increased. A similar behaviour is observable with sulphuryl chloride formation and decomposition.

Coehn and Becker (*Ber.* **43**, 130 (1910)) found that phosgene is decomposed at room temperature by ultra-violet light, a stationary state with about 4 % decomposition being reached in the total radiation of a mercury lamp. Bredig and Goldberg (*Z. physik. Chem.* **110**, 521 (1924)) noticed that, when mixtures of phosgene and hydrogen are illuminated by ultra-violet light, the decomposition of the former is almost complete, and hydrogen chloride is formed.

Bodenstein observed that the concentration of oxygen in an illuminated mixture of chlorine, carbon monoxide, and oxygen does not remain constant, this latter reacting with carbon monoxide to form

the dioxide. This reaction is photosensitized by chlorine, as neither of the components absorbs visible light. In mixtures rich in oxygen, the rate of formation of CO_2 is even faster than that of phosgene. The quantum yield in the photosynthesis of phosgene is high, and is of the order of 1000—1500 molecules per quantum absorbed.

The study of the thermal formation and decomposition of phosgene has led to a complete explanation of the mechanism of the thermal reaction. The thermal reactions show fewer complications than the photochemical one, oxygen and traces of moisture having no influence on their thermal velocities.

Christiansen (*Z. physik. Chem.* **103**, 99 (1923)), and later Bodenstein and Plaut (*Ibid.* **110**, 399 (1924)) showed that the thermal rates of formation and decomposition of phosgene can be represented by the equation.

$$+ \frac{d[\text{COCl}_2]}{dt} = K \sqrt{[\text{Cl}_2]} \left[\frac{1}{K_1} [\text{CO}][\text{Cl}_2] - [\text{COCl}_2] \right]$$

and derived this equation kinetically from the following reaction processes:—

- (1) $\text{Cl}_2 \rightleftharpoons 2 \text{Cl}$ } Thermal equilibria maintained during the re-
 (2) $\text{Cl}_2 + \text{Cl} \rightleftharpoons \text{Cl}_3$ } action.
 (3) $\text{Cl}_3 + \text{CO} \rightleftharpoons \text{COCl}_2 + \text{Cl}$ Process which determines the velocity.

Recently Bodenstein attempted to explain the kinetics of the photochemical formation of phosgene by means of the following intermediary processes, which are in some respects similar to those of the thermal processes:

- (1) $\text{Cl}_2 + h\nu \rightarrow \text{Cl}'_2 \dots\dots\dots (K_1)$
 (2) $\text{Cl}'_2 + \text{CO} \rightarrow \text{CO}' + \text{Cl}_2 \dots\dots\dots (K_2)$
 (3) $\text{Cl}_2 \rightarrow 2 \text{Cl} \dots\dots\dots (K_3)$
 (4) $\text{Cl}_2 + \text{Cl} \rightarrow \text{Cl}_3 \dots\dots\dots (K_4)$
 (5) $\text{Cl}_3 + \text{CO} \rightarrow \text{COCl}_2 + \text{Cl} \dots\dots\dots (K_5)$
 (6) $\text{Cl}_3 \rightarrow \text{Cl}_2 + \text{Cl} \dots\dots\dots (K_6)$
 (7) $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2 \dots\dots\dots (K_7)$

From these, the following equation can be deduced:

$$(1) + \frac{d[\text{COCl}_2]}{dt} = \frac{K_5 K_4 [\text{CO}][\text{Cl}_2]}{K_6 + K_5 [\text{CO}]} \sqrt{\frac{K_1 K_3 I_{\text{abs}}}{K_7 (K_2 [\text{CO}] + K_3)}}$$

and this equation becomes the same as that obtained experimentally for the moist gases at room temperatures, namely

$$(2) \quad + \frac{d[\text{COCl}_2]}{dt} = \frac{K_5 K_4}{K_6} \sqrt{\frac{K_1 K_3 I_{\text{abs}}}{K_7 K_2}} [\text{CO}] \cdot [\text{Cl}_2],$$

if we assume that K_6 is much greater than $K_5[\text{CO}]$ and $K_2[\text{CO}]$ than K_3 .

The kinetics of the reaction with dry gases, or at elevated temperatures, remain unexplained by Bodenstein's mechanism.

Cathala (*J. Chim. phys.* **24**, 663 (1927)) has investigated the formation of carbonyl chloride under the influence of rays from a gas-filled quartz mercury lamp. The gaseous mixture was prepared by decomposing purified carbonyl chloride at 800° . The progress of the reaction was examined by determining the proportion of combined and uncombined chlorine in the gaseous mixture after definite periods of illumination. The velocity of the reaction is best expressed by the equation

$$\frac{d[\text{COCl}_2]}{dt} = K[\text{CO}] \times [\text{Cl}_2],$$

which is the same as that found by Bodenstein (*Rec. trav. chim.* **41**, 585 (1922)) for the thermal synthesis of carbonyl chloride. Oxygen and carbon dioxide have a strong inhibiting effect on the photochemical reaction, but not on the thermal reaction. The retarding influence of carbon dioxide appears to be due to the oxygen produced by the decomposition of the carbon dioxide by ultra-violet light. If the photochemical synthesis is carried out at 357° , the carbon dioxide is again without effect, probably due to the destruction of the retarding effect at this temperature. The course suggested for the photochemical synthesis is the same as that adopted by Bodenstein for the thermal synthesis. (Compare Berthoud, *Réunion internationale de chimie physique*, p. 342, Paris, October 1928.)

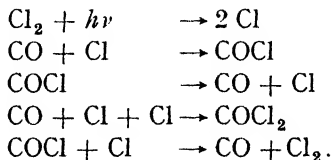
On the other hand, Bodenstein and Onoda (*Z. physik. Chem.* **131**, 153 (1928)) have stated that the course of the reaction at high temperatures is governed by the equation

$$\frac{d[\text{COCl}_2]}{dt} = \frac{KI[\text{Cl}_2]}{[\text{CO}]},$$

where I is the intensity of the light absorbed. The reaction, according

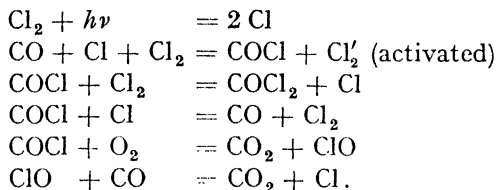
to Bodenstein and Onoda, is unaffected by oxygen. The main reaction between chlorine, carbon monoxide, and oxygen at the ordinary temperature results in the formation of carbon dioxide, whilst as the temperature is raised the quantity of carbonyl chloride increases, until at 300° , formation of carbon dioxide ceases. From 270° to 300° the velocity coefficient of the formation of carbonyl chloride is considerably influenced by hydrolysis of the reaction product by water vapour. At 400° simultaneous chemical and photochemical formation of carbonyl chloride may be observed by employing low pressures and intense irradiation. The equilibrium of the reaction in the dark is unaltered by illumination.

Very recently Bodenstein, Lenher, and Wagner (*Z. physik. Chem. B* **3**, 459 (1929)) have studied the reaction at the ordinary temperature and at pressures lower than 40 mm. The expression for the velocity coefficient obtained previously does not explain the observations at lower pressures, and it is found necessary to make different assumptions regarding the mechanism of the chemical change. It is suggested that in addition to the changes in the gas phase which result in the removal of chlorine atoms, there is at lower pressures a diffusion of COCl and Cl to the walls of the vessel, where they remain adsorbed until recombination occurs. The explanation of the mechanism of the reaction advanced before by Bodenstein and co-workers is regarded as unsatisfactory, and it is now assumed that the specific influence of carbon monoxide on the recombination of the chlorine atom can be expressed by the equation $\text{COCl} + \text{Cl} = \text{CO} + \text{Cl}_2$, and that direct recombination in the gas phase is negligible. This assumption leads to a simple explanation of the photochemical formation of carbonyl chloride at the ordinary temperature, the individual reactions being:



Very recently Lenher and Rollefson (*J. Amer. Chem. Soc.* **52**, 500 (1930)) have discussed the mechanism of the photochemical formation of phosgene. They have stated that the principal weakness in the scheme of Bodenstein, Lenher, and Wagner (*Z. physik. Chem. B* **3**, 459 (1929)) is that it disregards the formation of phosgene by the action of chlorine on COCl. They suggest the following scheme for the photo-

chemical formation of phosgene at room temperature:



The authors believe that the above scheme is preferable to that advocated by Bodenstein, Lenher, and Wagner, because it rests on fewer assumptions than that of Bodenstein and collaborators.

Schultze (*Z. physik. Chem.* B 5, 368 (1929)) has stated that the photochemical formation of carbonyl chloride from intensively dried chlorine and carbon monoxide at one atmospheric total pressure follows the same relation as when moist gases are used. The temperature coefficient for a 10° rise of temperature between 15° and 50° has the value 0.9. Oxygen retards the reaction, due to the formation of carbon dioxide. Hence it appears that the photochemical formation of carbonyl chloride is almost as complicated as the photosynthesis of hydrochloric acid, since there is so much difference of opinion amongst different investigators.

OXALIC ACID AND CHLORINE.

This reaction has been investigated by Bhattacharya and Dhar (*J. Chim. phys.* 26, 556 (1929)), and is interesting because both the reacting substances are photosensitive. In absence of hydrochloric acid the reaction is too quick to be measured.

The changes in the concentration of chlorine were determined by adding *KI* and titrating with a standard thiosulphate solution.

From the following results it will be observed that Einstein's law of photochemical equivalence is not exactly applicable to this reaction. The quantum efficiency increases with temperature and the frequency of the incident radiation.

The relation between intensity and velocity varies from $\frac{3}{2}$ to $\frac{1}{3}$, depending upon the velocities of the thermal and photochemical reactions.

When the velocity of the thermal reaction has been decreased considerably by adding a concentrated solution of hydrochloric acid, and the reaction mixture is exposed to sunlight and the reaction

N/5 oxalic acid and N/75 chlorine in presence of 1.25 N HCl.
 5 c.c. 10 c.c. 5 c.c.

Condition	Temperature in °C	K_1 Mono-molecular	Temperature Coefficient after deducting the dark reaction	Total order	Quantum efficiency
Dark	15 25 35	0.0119 0.0351 0.1018	2.95 2.90	Bimolecular	
N/10 $\text{H}_2\text{C}_2\text{O}_4$	15 25 35	0.00598 0.0173 0.0484	2.90 2.82		
Region $\lambda = 4725 \text{ \AA}$	15 25 35	0.0186 0.0505 0.134	2.3 2.19		4.5 8.6 16.9
$\lambda = 5650 \text{ \AA}$	15 25 35	0.0168 0.0468 0.127	2.4 2.28		3.8 7.2 12.6
$\lambda = 7304 \text{ \AA}$	15 25 35	0.0149 0.0426 0.120	2.5 2.42		2.1 4.9 8.6
$\lambda = 8500 \text{ \AA}$	15 25 35	0.0131 0.0384 0.111	2.75 2.72		0.63 0.75 0.94

highly accelerated, the relation between intensity and velocity tends to be $\frac{1}{3}$. This relation goes on increasing as the acceleration of light reaction over the corresponding thermal reaction is decreased. It increases so much as to show a relation $\frac{3}{2}$ in the region $\lambda = 7304 \text{ \AA}$. Here the source of light is not intense and the photochemical acceleration is very small, and, the concentration of hydrochloric acid being less, the velocity of the reaction in the dark is quite high. The total result is that the acceleration due to light is not marked in comparison with the dark reaction, and the ratio between intensity and velocity rises to $\frac{3}{2}$.

CINNAMIC ACID AND CHLORINE.

Nazarov (*J. Russ. phys. Chem.* **47**, 943 (1915)) was the first to study the reaction between chlorine and cinnamic acid in carbon tetrachloride solution, and found that the temperature coefficient of the reaction is 1.4 in white light.

Recently Basu (*J. Indian Chem. Soc.* **6**, 341 (1929)) has investigated the velocity of this reaction in radiations of different wavelengths, and the temperature coefficient and the quantum yield. The reaction appears to be unimolecular with respect to chlorine in light, as well as in the dark, and the values of the unimolecular coefficient remain unaffected by change in the concentration of cinnamic acid. The following temperature coefficients and quantum yields were obtained with radiations of different wavelengths:

Wavelength in Å	3665	4040	4360
Temperature Coefficient (between 22.6° and 32.6°)	1.1	1.29	1.38
Quantum yield	7	4	2

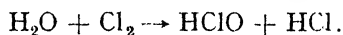
No fluorescence was observed with a carbon tetrachloride solution of chlorine. The author has explained his results from the view point of Franck that by the absorption of radiations shorter than 4785 Å a chlorine molecule undergoes a primary dissociation into a normal and an excited atom. Compare Dymond (*Z. Physik* **34**, 553 (1925)) and Kuhn (*ibid* **39**, 77 (1926)). The excited chlorine atom is supposed to combine with a cinnamic acid molecule to form a monochloride which carries the energy of excitation.

DECOMPOSITION OF CHLORINE WATER.

In 1785 Berthollet stated that chlorine water is gradually decomposed by exposure to light, forming aqueous HCl and oxygen. Wollaston noted that the chemically active rays are the most refrangible. Sir Humphry Davy in 1812 also reported that the rays at the violet end of the spectrum are more active in promoting the decomposition of chlorine water than the other rays. De Saussure (1799) found that the rate of decomposition depends on the intensity of the light, and tried to measure the quantity of oxygen which is developed in this reaction, utilizing this reaction as a kind of photometer to measure the action of light. Draper (*Fortschritte der Physik*, 1845, 276) came to the conclusion that this reaction showed both an induction period and a marked after effect. Recently Allmand and co-workers (*J. Chem. Soc.* **127**, 822 (1925)) attribute Draper's results to the supersaturation of the liquid by oxygen formed during illumination, and its continued evolution in the dark. Pedler (*J. Chem. Soc.* **57**, 613 (1890)) showed that a solution of chlorine in water more concentrated than one molecule of chlorine in 64 molecules of water had not decomposed perceptibly after two months' exposure to sunlight (tropical). With increasing

dilution, the percentage decomposition of chlorine water becomes greater and greater. In 1885 Wittwer (*Pogg. Ann.* **94**, 597 (1885)) concluded that the velocity of the disappearance of chlorine is proportional to the intensity of the radiation, and can be expressed by a unimolecular reaction velocity equation. This conclusion is not in agreement with the observations of Bunsen and Roscoe (*Pogg. Ann.* **96**, 373 (1855)), and Billitzer (*Chem. Z.* **30**, 1131 (1906)), who reported that the velocity is not directly proportional to the light intensity, and that the reaction is autocatalytic. On the other hand, Benrath and Tüchel (*Z. wiss. Phot.* **13**, 383 (1913)) represented their observations by an unimolecular equation with fairly satisfactory results.

All earlier investigators of the chlorine water decomposition assumed that HCl and O₂ were the only products of reaction, until Popper (*Lieb. Ann.* **227**, 661 (1885)), Gore (*Chem. News* **57**, 184 (1888)), Pedler (*J. Chem. Soc.* **57**, 613 (1890)), and Klimenko (*Ber.* **28**, 2558 (1895)), proved the formation of chloric acid, which is formed from hypochlorous acid, the first product according to the equation



Gore also reported the formation of H₂O₂, and Richardson (*J. Chem. Soc.* **59**, 536 (1891)) suggested that the evolved oxygen is ozonized, and Billitzer reported the formation of perchloric acid.

Klimenko believed that the products formed on dissolving chlorine in water are shown by the following equation: $\text{Cl}_2 + \text{H}_2\text{O} = \text{HClO} + \text{HCl}$, and that the HClO partly undergoes the following change: $3\text{HClO} = 2\text{HCl} + \text{HClO}_3$. His opinion that hypochlorous acid is the only photochemically active component was supported by Jakowkin (*Z. physik. Chem.* **29**, 621 (1899)), and Dawson (*Z. wiss. Phot.* **14**, 213 (1914)). On the other hand, Billitzer, and Benrath and Tüchel believed that it is the non-hydrolyzed chlorine molecule which becomes activated on absorbing light. Recently Benrath and Schaffganz (*Z. physik. Chem.* **103**, 139 (1922)) advanced the view that the ion ClO is mainly responsible for the photosensitivity of chlorine water.

According to Klimenko and Pekatoras (*Z. physik. Chem.* **4**, 483 (1889)), the reaction proceeds to a quantitative completion, and no stationary state is formed on illumination. HCl and chlorides retard the reaction. Benrath and Tüchel claimed that only pure chlorine water decomposes quantitatively, while in presence of HCl or chlorides the reaction is incomplete. Further work is necessary to settle this point. According to Benrath and Tüchel the temperature coefficient of the reaction is 1.4. Milbauer (*Z. physik. Chem.* **86**, 564 (1914))

observed a retarding action of salts of heavy metals on the decomposition of chlorine water, these acting as internal light filters. On the other hand, he observed that bromine accelerates the decomposition of chlorine water, and chlorine that of bromine water.

Allmand, Cunliffe, and Maddison (*J. Chem. Soc.* **127**, 822 (1925)) investigated the decomposition of chlorine and hypochlorous acid solutions in quartz vessels under the influence of the total radiation from a mercury lamp. These authors state that neither H_2O_2 nor perchloric acid is formed in either of these decompositions, the products being HCl , HClO_3 and O_2 . The yields of chloric acid were the same in monochromatic light of wavelengths 4360, 3660 and 3230 Å, and were unaffected by solutions of sulphates, and variations in the concentrations of chlorine water and hypochlorous acid, but were decreased by HCl or chlorides. With HClO and sodium acetate, the formation of HClO_3 and CCl_3COOH is observed.

Allmand and co-workers suggested that hypochlorous acid is considerably more photosensitive than the chlorine molecule, and that the primary action is $\text{HClO} + \text{light} \rightarrow \text{HCl} + \text{O}$. The oxygen atoms formed either combine to form oxygen molecules, or oxidize HClO to HClO_3 . Since the equilibrium $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{HClO}$ is established in the system, an addition of H ions or Cl ions will decrease the concentration of HClO and thus diminish the yield of HClO_3 , and also the photochemical decomposition will be retarded. Addition of the sodium salt of a weak acid increases the yield by the removal of H ions. Similarly, HgCl_2 increases the yield of HClO_3 by removing chlorine ions due to the formation of the HgCl_4 ion. Allmand and co-workers state that their explanation is not quantitative, and conclude that apart from HClO , chlorine molecules take some part in the reaction mechanism.

Allmand, Cunliffe, and Maddison (*J. Chem. Soc.* 655 (1927)) have measured the coefficients of light extinction for the range 3650—4360 Å for hypochlorous acid and chlorine water. The values of the extinction coefficient for chlorine in solution are very close to those for gaseous chlorine. The quantum efficiency at 3650 Å for the decomposition of chlorine water is about 2, and it varies only slightly over the range 3130 to 4360 Å, but is greatly reduced by the addition of certain strong electrolytes, notably hydrochloric acid.

CHLORINATION OF BENZENE. — Slator (*Z. physik. Chem.* **45**, 540 (1903)), studying the photochlorination of benzene, observed the proportionality of the reaction velocity to the square of the chlorine

concentration. Luther and Goldberg (*ibid.* **56**, 43 (1906)) demonstrated that Slator's results were due to a varying amount of oxygen dissolved in benzene, the reaction velocity being proportional to the chlorine concentration. Oxygen shows a strong retarding influence on the reaction, its active mass being used up by its action on benzene in light. The retarding influence of oxygen is very marked, the reaction velocity in benzene which has been freed from oxygen by evacuation being about 75 times faster than in benzene saturated with oxygen at 3.5 atmospheres.

Bodenstein (*ibid.* **85**, 329 (1913)) calculated the photochemical yield of the chlorination of benzene free from oxygen to be as high as 10^6 molecules per quantum of light absorbed.

From the researches of Slator (*loc. cit.*) on the chlorination of benzene in the presence of several catalysts, and of light, we get the following interesting results:

Catalyst	ICl	SnCl ₄	FeCl ₃	Light
Temp. coefficient	1.05	1.5	2.5	1.5

Of the three positive catalysts (chemical) used in this reaction the order of efficiency is the following: $\text{ICl} > \text{SnCl}_4 > \text{FeCl}_3$. It is clear that the greater the acceleration produced by a given chemical catalyst, or light, the smaller is the value of the temperature coefficient.

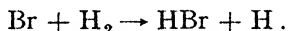
CHLORINATION OF TOLUENE.—Luther and Goldberg (*loc. cit.*) showed that oxygen exerts a retarding influence on the photochemical chlorination of toluene, xylene, and acetic acid. Book and Eggert (*Z. Elektrochem.* **34**, 521 (1923)) observed that chlorine reacted with toluene in light even at -80° , the velocity of thermal reaction being negligible at this temperature. The chlorination took place in the side chain, about 26 molecules of chlorine reacting per absorbed quantum of light.

CHLORINATION OF ALIPHATIC COMPOUNDS.—Benrath and Hertel (*Z. wiss. Phot.* **23**, 30 (1924)) investigated the chlorination of saturated aliphatic compounds dissolved in CCl_4 . An induction period which was shorter for pure substances was noticed. A unimolecular reaction with respect to chlorine was observed in the case of propionic acid, whereas with acetic acid the velocity was better expressed by the equation $K \log t = [\text{Cl}_2]_0 - [\text{Cl}_2]_t$. In the case of acetic acid, the reaction stops when one hydrogen atom is substituted by chlorine, but in propionic and butyric acids two hydrogen atoms are substituted by chlorine, and the reaction proceeds in two distinct steps, the monochlorinated product being the first to be formed.

CHAPTER VII.

Photochemical Reactions with Bromine as a Reacting Substance.

COMBINATION OF HYDROGEN AND BROMINE. — The light sensitivity of a mixture of bromine and hydrogen was first observed by Kastle and Beatty (*J. Amer. Chem. Soc.* **20**, 159 (1898)). They observed that hydrogen and bromine unite completely in sunlight at 196°, but not in darkness; the amount of combination is approximately proportional to the time of exposure. At 100°, there is a slight formation of HBr in sunlight, though there is no reaction even in sunlight at the ordinary temperature. Coehn and Stuckard (*Z. physik. Chem.* **91**, 722 (1916)) observed a quantitative formation of hydrogen bromide at 270°, in the light absorbed by bromine. Miss Pusch (*Z. Elektrochem.* **24**, 336 (1918)) observed a quantum yield of 0.001 molecule per quantum with this reaction at room temperature. Nernst explains this low yield from the view point of the formation of bromine atoms on illumination, and on the thermodynamic impossibility of the reaction



Bodenstein and Lütkemeyer (*Z. physik. Chem.* **121**, 127 (1926)) studied this reaction quantitatively at 160° to 218° in total radiation from a point-o-lite lamp. The reaction was followed photometrically. The velocity of the reaction with or without the addition of HBr follows the relation:

$$\frac{d[\text{HBr}]}{dt} = K \sqrt{I_{\text{abs}}} \frac{[\text{H}_2]}{1 + \frac{[\text{HBr}]}{10[\text{Br}_2]}}.$$

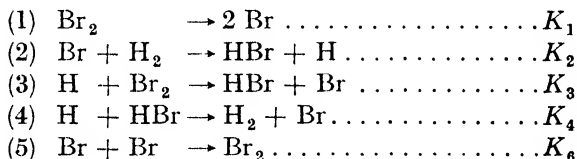
The equation shows that the reaction is proportional to the square root of the light absorbed, is retarded by hydrogen bromide, and is proportional to the concentration of the hydrogen molecules. temperature coefficient for a ten degree rise between 160° to 218°

The thermal reaction at 228° to 302° was investigated by Bodenstein and Lind (*Z. physik. Chem.* **57**, 168 (1907)) in order to throw light on the photochemical process. A knowledge of the kinetic mechanism of the thermal reaction enabled Bodenstein to predict the kinetics of the process and to obtain some important results for the general theory of chemical reactions in the gaseous phase. The velocity of the thermal reaction could be represented by the following empirical formula:

$$+\frac{d[2\text{HBr}]}{dt} = \frac{K[\text{H}_2]\sqrt{[\text{Br}_2]}}{5 + \frac{2[\text{HBr}]}{[\text{Br}_2]}}$$

Bodenstein and Lind suggest that bromine atoms and not molecules reacted with hydrogen to form HBr.

The full theory of this reaction was given independently by Christiansen (*Danske vid. Math. Phys. Medd.* I, 14 (1919)), Herzfeld (*Z. Elektrochem.* **25**, 301 (1919)), and Polanyi (*ibid.* **26**, 50 (1920)). These authors suggest the following sequence of reactions:



The kinetic interpretation of these equations, and the assumption that the concentrations of bromine and hydrogen atoms are constant, led to the final expression for the velocity of the reaction, and this is practically identical with the empirical equation of Bodenstein and Lind:

$$\frac{d[\text{HBr}]}{dt} = \frac{2K_2[\text{H}_2]\sqrt{\frac{K_1[\text{Br}_2]}{K_6}}}{1 + \frac{K_4[\text{HBr}]}{K_3[\text{Br}_2]}}$$

For the photochemical reaction Bodenstein suggested that the primary action of light consisted in the dissociation of a bromine molecule into atoms, two atoms being formed for each quantum absorbed. Subsequent reactions are supposed to be identical with those of the thermal reaction. Putting the number of absorbed quanta per second = a and writing the rate of reaction in the usual manner, we arrive at the

equation identical with that derived by Bodenstein and Lind:

$$\frac{d[\text{HBr}]}{dt} = \frac{2 K_2 [\text{H}_2] \sqrt{\frac{a}{K_6} [\text{Br}_2]}}{1 + \frac{K_4 [\text{HBr}]}{K_3 [\text{Br}_2]}}$$

From the calculated kinetic equations it will be seen that the rate of the photochemical as well as that of the thermal reaction is proportional to the stationary concentration of bromine atoms, and hence:

$$(\text{Br})_{\text{light}} = (\text{Br})_{\text{dark}} \times \left(\frac{\text{light velocity}}{\text{dark velocity}} \right).$$

The results show that the concentration of bromine atoms in light is about 300 times larger than in the dark. The number of bromine atoms formed per second is equal to twice the number of absorbed quanta.

In studies of the kinetics of those photochemical reactions which are accompanied by thermal reactions of measurable velocity, the assumption has almost tacitly been made that each of the reactions, although taking place simultaneously with the other, does not influence its velocity. Consequently, the rate of a photochemical reaction is usually determined by subtracting the dark reaction velocity from the total velocity observed in light. It can, however, be easily demonstrated that this additive relation is not valid for the combination of bromine and hydrogen.

W. Jost (*Z. physik. Chem.* **134**, 92 (1928)) has stated that the reaction between hydrogen and bromine, illuminated by light of wavelength corresponding with the region of the bromine spectrum showing absorption bands, and with that corresponding with the continuous spectrum, shows that the velocity coefficient is of the same order of magnitude in the two cases. Jost and Jung (*ibid.* **B. 3**, 83 (1929)) have deduced a formula based on the assumption of triple collisions, and, according to this formula, the velocity of the photo-synthesis of hydrogen bromide should depend on the total pressure. The experiments of Bodenstein and Lütkemeyer (*ibid.* **114**, 208 (1924)) do not agree with this conclusion. Jost and Jung have carried out experiments to test the validity of their equation, and it is found that the reaction velocity is inversely proportional to the square root of the total pressure. Moreover, Jost (*ibid.* **B. 3**, 95 (1929)) has stated that the activated bromine atoms formed primarily in the light behave

like inactive atoms, and become deactivated before entering into the reaction. The walls of the vessel exert a characteristic effect on the reaction velocity.

Recently Armour and Ludlam (*Proc. Roy. Soc. Edin.* **49**, 91 (1929)) have exposed a mixture of hydrogen and bromine to light of the shortest wavelength (1850 Å) possible with quartz apparatus, using an aluminium spark. At the equilibrium concentration, it has been found that somewhat less than one per cent by weight of bromine combines to form hydrogen bromide.

Briers and Chapman (*J. Chem. Soc.* 1802 (1928)) have recently studied the influence of light intensity on the photochemical combination of bromine and hydrogen, and have concluded that the reaction velocity is proportional to a power of the light intensity, which varies between $\frac{1}{2}$ and 1, and is always greater the weaker the light. From their experiments, they have observed that the velocity of disappearance of the "catalyst, excited bromine molecules or bromine atoms", which causes the reaction, is given by the combination of a uni- and a bi-molecular reaction,

$$-\frac{dA}{dt} = C_1 A^2 + C_2 A \dots,$$

where A is the concentration of the catalyst, and that its mean life is about 0.063 sec. These results of Briers and Chapman have been verified by Bodenstein, Jost, and Jung (*J. Chem. Soc.* 1153 (1929)).

In publications from these laboratories, we have shown that in many reactions involving bromine, and where a bromide or hydrobromic acid is generated, the velocity of the photobromination is proportional to a power of the light intensity which varies between $\frac{1}{4}$ and 2, depending on the ratio of the photochemical and thermal reaction velocities. Hence we are convinced that in the photochemical combination of bromine and hydrogen, also, the velocity will be proportional to a power of the light intensity, which will be less than $\frac{1}{2}$ when the light is very intense, and is highly absorbed by the mixture of hydrogen and bromine. On the other hand, when the light intensity is feeble, and the radiation is not much absorbed by the mixture, the factor may even go up to 2. Experimental work is in progress to verify these deductions.

BROMINATION OF BENZENE.

Recently Meidinger (*Z. physik. Chem. B.* **5**, 29 (1929)) has studied the bromination of benzene in light at low concentrations of bromine,

using carbon tetrachloride as a diluting solvent. It has been observed that bromine can be substituted directly in the ring, with the formation of monobromobenzene, or the double linkings can be broken with the generation of benzene hexabromide. It has been assumed that one light quantum liberates two bromine atoms, which are the active agents in the bromination. The velocity of the reaction appears to be independent of the bromine concentration, and of the wavelength of the light used. The temperature coefficient of the reaction decreases from 1.6 to unity with decreasing concentration of benzene.

BROMINATION OF TOLUENE.

Luther and Goldberg (*loc. cit.*) thought that the bromination of toluene was not retarded by oxygen, but Bruner and Czernecki (*Bull. Accad. Sci. Cracow* (A) 576 (1910)) demonstrated the retarding influence of oxygen on this reaction. The inhibiting influence of oxygen is reduced by the presence of iodine. In absence of oxygen, the rate of reaction is proportional to the intensity of the incident radiation and to the concentration of toluene, and is independent of the bromine concentration, if the absorption of light by the latter is complete. The bromination occurs in the side chain, and has a high temperature coefficient of 1.8, whereas the thermal reaction shows a still higher value 4.0. Bodenstein calculated the quantum yield of this reaction to be as high as 10^6 in absence of oxygen.

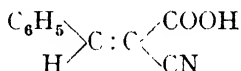
The bromination of toluene was also studied by Andrich and Le Blanc (*Z. Elektrochem.* 20, 543 (1914); *Z. wiss. Phot.* 15, 148 (1915)) who observed an oxidation of HBr formed by oxygen present in the system.

Some very interesting results were obtained by Andrich and Le Blanc regarding the influence of light of wavelengths shorter than 3500 Å, which was ineffective in causing the reaction, though it was strongly absorbed by the solution of bromine in toluene. A comparison of the absorption spectra showed that toluene alone absorbs light only below 3000 Å, but bromine dissolved in hexane has a pronounced minimum of absorption at 3200 Å. A similar absorption minimum of gaseous bromine was also observed by Coehn and Stuckard (*Z. physik. Chem.* 91, 722 (1916)). On the other hand, a solution of bromine in toluene shows a minimum, the absorptive capacity uniformly increasing towards shorter wavelengths. Andrich and Le Blanc suggest that the change in the absorption spectrum of bromine is due to the formation of molecular compounds with toluene, these absorbing the

ultra-violet rays, but not reacting. These results appear very peculiar, and need further confirmation. In support of their view, Andrich and Le Blanc showed that the bromination of hexane was sensitive to all wavelengths absorbed by bromine, in agreement with the normal absorption spectrum of this bromine solution.

BROMINATION OF α -PHENYL CINNAMONITRILE.

Plotnikoff (*Z. wiss. Phot.* **19**, 1 (1919)) enumerates a large number of brominations of unsaturated carbon compounds. The bromination of α -phenyl cinnamionitrile



dissolved in CCl_4 was studied at 7° , in radiation of wavelength 4360 Å, and was investigated in detail. The bromination product being unstable at this temperature, a dark-light stationary state is reached, for which Plotnikoff derives the equation

$$K = I_0 \frac{(1 - e^{-i[\text{Br}_2]})}{[\text{C}_1 \text{Br}_2]} \times \text{C}_1$$

where $[\text{Br}_2]$, $[\text{C}_1]$, and $[\text{C}_1\text{Br}_2]$ are the concentrations of bromine, of nitrile, and of the bromination product, and i is the light absorption coefficient of bromine.

The experiments of Berthoud and Nicolet (*Helv. Chim. Acta* **10**, 417 (1927); *J. Chim. phys.* **25**, 40 (1928)) indicate that the stationary state can be represented by the equation:

$$\frac{[\text{Br}_2] (K_1 [\text{C}_1] + K_2 [\text{C}_1 \text{Br}_2])}{[\text{C}_1 \text{Br}_2]} = K.$$

The constant K was found to be independent of the light intensity. In agreement with this observation, Berthoud and Nicolet concluded that their results entirely disagree with those of Plotnikoff, and found that the decomposition of the brominated nitrile is not a thermal reaction, as was assumed by Plotnikoff, but is photosensitized by bromine. Berthoud states that light absorption by bromine being complete, the rate of bromination is represented by the equation

$$+ \frac{d[\text{C}_1 \text{Br}_2]}{dt} = K \sqrt{I_0} [\text{Br}_2],$$

if the concentration of the bromination product is small. The opposed reaction, according to Berthoud, follows the equation

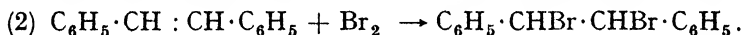
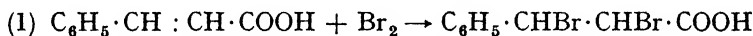
$$-\frac{d[\text{C}_1\text{Br}_2]}{dt} = K_2 \sqrt{I_0} \frac{[\text{C}_1\text{Br}_2]}{[\text{C}_1]}.$$

Berthoud interprets the equations in which the square root of the light intensity is included, to signify that on illumination a primary dissociation of bromine into atoms takes place.

BROMINATION OF CINNAMIC ACID AND STILBENE.

In recent years these reactions have been investigated by numerous workers, notably by Berthoud and Béranek (*J. Chim. phys.* **24**, 213 (1927)), and Ghosh and co-workers (*J. Indian Chem. Soc.* **2**, 261 (1926), **4**, 409, 553 (1927)).

The reactions take place according to the following equations:



Berthoud and Béranek have studied both the reactions in CCl_4 solution, in blue light, and find that the same relations are applicable to both cases. When absorption is completed by the use of concentrated bromine, the velocity is proportional to the bromine concentration and practically independent of the concentration of cinnamic acid or stilbene, and to the square root of the light intensity. Hence the velocity when the absorption is complete can be represented by

$$-\frac{d[\text{Br}_2]}{dt} = K I_0^{\frac{1}{2}} [\text{Br}_2].$$

When the absorption is feeble, the reaction ceases to be unimolecular with respect to bromine, and the following equation represents the velocity:

$$-\frac{d[\text{Br}_2]}{dt} = K I_0^{\frac{1}{2}} [\text{Br}_2],$$

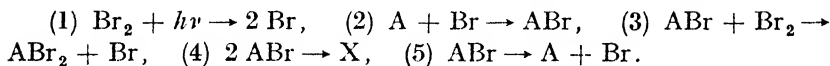
which on integration becomes

$$K = \frac{1}{2(t_2 - t_1)} \left[(a - x_2)^{-\frac{1}{2}} - (a - x_1)^{-\frac{1}{2}} \right].$$

The experimental results agree with the above relation. Berthoud and Béraneck (*J. Chim. phys.* **24**, 213 (1927)) explain the observed results on the following assumptions:

- (a) Light dissociates the molecules of bromine.
- (b) An atom of bromine unites with a molecule of cinnamic acid or stilbene to form an unstable monobromo compound ABr.
- (c) This unstable compound reacts with a molecule of bromine forming the dibromoderivative, and re-forms atomic bromine.
- (d) The quantum yield is about 30. Hence it is assumed that atomic bromine or activated molecules of ABr disappear in certain reactions but are regenerated, as the quantum yield is not infinite.
- (e) It can also be admitted that the unstable molecules of ABr can decompose on collision with the solvent molecules.

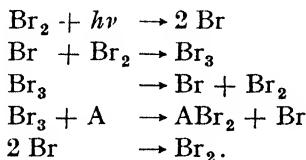
The various processes are represented as follows:



On applying the law of mass action to the secondary reactions, and that of Grotthus-Draper to the dissociation of bromine, one gets the same relations as are obtained empirically.

Ghosh and co-workers, working in blue (4940—4580 Å) and green (5400 to 5050 Å) lights, with carbon tetrachloride and disulphide as solvents, have drawn the following conclusions:

(1) There is a regular diminution in the velocity coefficients with increase in time. This has been explained by assuming the following mechanism for the reactions:



(2) The temperature coefficient of the light reaction increases with the wavelength of the incident light.

(3) In blue light the velocity coefficients vary as the square root of the intensity of the incident radiation, but the increase is greater in green light.

(4) The velocity of the reaction depends upon the concentration of the acceptor molecules.

(5) The quantum yield in the bromination of cinnamic acid in carbon tetrachloride is 43 (4880 Å) and 22 (5330 Å). In carbon di-

sulphide, the yield is 156 (4880 Å) and 101 (5330 Å). With stilbene in CCl_4 the quantum yield is 34 (4880 Å) and 16 (5330 Å), and in CS_2 it is 99 (4880 Å) and 52 (5330 Å).

These authors have observed that a period of induction and the phenomenon of "after effect" occur in these brominations.

Recently Plotnikoff (*J. Chim. phys.* **26**, 44 (1929)) has concluded, from a critical review of the literature relating to the photochemical reactions of bromine and iodine, that the experimental data are too incomplete, and the discrepancies too pronounced, for it to be possible to reach any definite conclusions as to the reaction mechanism (compare Berthoud, *J. Chim. phys.* **26**, 333 (1929)).

Very recently Purkayastha and Ghosh (*Z. Physik. Chem. B.* **7**, 276 (1930)) have stated that the reaction between bromine and organic oxyacids is bimolecular with respect to bromine in the dark, and unimolecular in light. The arguments advanced by the authors are not convincing. If the retarding influence of hydrobromic acid, which is a product of the chemical changes, is taken into account, the reaction in the dark appears to be unimolecular with respect to bromine.

LACTIC ACID AND BROMINE.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916)) showed that the reaction between bromine and lactic acid was highly accelerated by light. Recently Purkayastha (*J. Indian Chem. Soc.* **6**, 361, 375 (1929)) has studied the temperature coefficient and quantum yield of this reaction, as well as those of oxidations of other organic acids by bromine. The following results have been obtained by him:

Wavelength of light used = 4700 Å.

Acid	Quantum yield
0.46 M lactic	15
0.265 M mandelic	13
0.253 M citric	3
0.08 M phenyl lactic	13

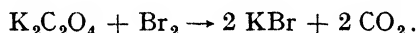
The temperature coefficients between 22° and 32° are 1.68 for lactic and 1.8 for mandelic in the same light (4700 Å). The velocities of oxidation of lactic, citric, and mandelic acids by bromine are almost proportional to the square root of the light intensity. Most of these reactions show induction period and after effect.

Purkayastha has also determined the extinction coefficient of the Br_3 ion for radiations of wavelengths 5360, 5460, and 5790 Å. He has reported that the oxidations of lactic and mandelic acids by bromine, which appear to be unimolecular, become zero-molecular in presence of a bromide in light. He has explained his results on the assumption that only the fraction of light absorbed by bromine molecules is photochemically active, and that the energy absorbed by Br_3 ions is photochemically inactive.

POTASSIUM OXALATE AND BROMINE.

The reaction between potassium oxalate and bromine has been investigated by Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916)), and by Bhattacharya and Dhar (*J. Indian Chem. Soc.*, **6**, 523 (1929)). The changes in the concentration of bromine were determined by adding KI and titrating with a standard thiosulphate solution.

The reaction takes place according to the equation:



N/10 potassium oxalate and N/100 bromine (100 c.c. Br_2 dissolved in 2 gms. KBr).

Condition	Temperature in °C	K_1 Mono-molecular	K_1 After deducting the dark reaction	Temperature Coefficient	Quantum efficiency
Dark	20	0.00450		5.61	
	30	0.0256		5.20	
	40	0.133			
$\lambda = 4725 \text{ Å}$	20	0.0348	0.0303	2.65	79
	30	0.106	0.0804	2.56	170
	40	0.339	0.206		320
$\lambda = 5650 \text{ Å}$	20	0.0309	0.0264	2.78	66.6
	30	0.0991	0.0735	2.63	107
	40	0.326	0.193		266
$\lambda = 7304 \text{ Å}$	20	0.0248	0.0203		54.4
	30	0.0874	0.0618	3.04	86.8
	40	0.320	0.187	3.0	184
$\lambda = 8500 \text{ Å}$	20	0.00819	0.00369	4.42	34.3
	30	0.0419	0.0163	4.30	68.4
	40	0.203	0.0700		110

Berthoud and Bellenot (*Helv. Chim. Acta.* **7**, 307 (1924)) have also investigated the kinetics of this photochemical reaction, and have

stated that the velocity of the reaction can be represented by the following relation:

$$-\frac{d[\text{Br}_2]}{dt} = KI_0^{\frac{1}{2}} [\text{Br}_2]^{\frac{1}{2}} [\text{C}_2\text{O}_4\text{K}_2] \text{ (when the absorption is feeble),}$$

$$-\frac{d[\text{Br}_2]}{dt} = KI_0^{\frac{1}{2}} [\text{C}_2\text{O}_4\text{K}_2] \text{ (when the absorption is total).}$$

Light Absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	0.02	0.04	0.09	0.13	0.19	0.25	0.30
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	0.42	0.57	0.67	0.71	0.78	0.85	0.93

The relation between intensity and velocity of this reaction varies from 1 to $\frac{1}{2}$ according to the thermal and photochemical reaction velocities. The dark reaction was varied by varying the amount of KBr. The source of light was also varied.

TARTARIC ACID AND BROMINE.

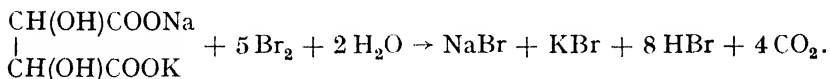
(Compare Dhar, *Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916).)

Ghosh and collaborators (*J. Indian Chem. Soc.*, **2**, 165 (1925)); **5**, 342, 361 (1928)) have shown that the reaction between aqueous bromine and tartaric acid is negligible in the dark. The light reaction (in the region 4500—4900 Å) has a long induction period, high quantum yield, and a temperature coefficient about 2 for a 10° rise of temperature. At constant bromine concentration increase of tartaric acid concentration results in an increase of the induction period, whilst at constant tartaric acid concentration increase of bromine concentration produces a small reduction in the induction period, but a considerable diminution of the unimolecular velocity coefficient. Sodium hydrogen tartrate greatly accelerates the reaction, and decreases the induction period. When hydrogen bromide, which is a product of the reaction, and which markedly retards the reaction, is added at the commencement of the reaction, the velocity coefficient of the reaction remains nearly constant with the progress of the change.

The mechanism of the reaction is assumed to be the atomization of bromine molecules by light absorption, and a combination of some of the bromine atoms with the oxygen present in the system. The remaining bromine atoms produce photobromination of the tartaric acid. In the initial stages, a proportion of the bromine atoms is used up in destroying the photoinhibitors.

ROCHELLE SALT AND BROMINE.

The photochemical reaction between bromine and rochelle salt has been studied by Mukerji and Dhar (*J. Phys. Chem.*, **33**, 850 (1929)). The change takes place according to the equation:



It is seen that owing to the gradual increase in the concentration of the hydrogen ions, the reaction is greatly retarded, and to avoid that difficulty some sodium acetate is added to the reacting system.

N/12.23 rochelle salt, N/121.2 bromine, and N/6.6 sodium acetate.

Condition	Temperature in °C	K_1 Mono-molecular	Temperature Coefficient after deducting the dark reaction K_{30}/K_{20}	Quantum Efficiency
Dark	20	0.00372	3.28	—
	25	0.00674		
	30	0.0122		
$\lambda = 5650 \text{ \AA}$	20	0.00998	2.03	33.4
	25	0.01426		36.8
	30	0.0203		53.3
$\lambda = 7304 \text{ \AA}$	20	0.00958	2.08	24.4
	25	0.01746		26
	30	0.0199		59

Einstein's law of photochemical equivalence is not applicable to this reaction. The quantum yield increases with temperature and the frequency of the incident radiation.

The relation between intensity and velocity of the reaction varies from $\frac{3}{2}$ to $\frac{1}{3}$, according to the velocities of the thermal and photochemical reactions.

METHYL ALCOHOL AND BROMINE.

The photochemical reaction between methyl alcohol and bromine has been studied by Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916)) and Dhar and Bhattacharya (*Z. anorg. u. allg. Chem.* **176**, 372 (1928)). The following are the experimental results:—

N/101.7 bromine and 43% methyl alcohol 10 c.c. each

Condition	Temperature in °C	K_1 Mono- molecular	Temperature Coefficient	Quantum Efficiency
Dark	20	0.00325	2.5	
	30	0.0080	2.45	
	40	0.0196		
$\lambda =$ Sunlight	20	0.0412	1.99	144
	30	0.0837	1.91	444
	40	0.165		1118
$\lambda = 4725 \text{ \AA}$	20	0.00479	2.4	5.5
	30	0.0117	2.27	11.4
	40	0.0280		32.2
$\lambda = 5650 \text{ \AA}$	20	0.00513	2.34	5.5
	30	0.0124	2.2	7.4
	40	0.0293		22.1
$\lambda = 7304 \text{ \AA}$	20	0.00453	2.42	3.65
	30	0.0111	2.35	6.8
	40	0.0269		16.7

The quantum efficiency increases with temperature and the frequency of the incident radiation. The quantum yield is very great in sunlight.

The temperature coefficients in light have been calculated after deducting the dark reaction. The temperature coefficient increases with the decrease in the velocity of the reaction.

The reaction between bromine and methyl alcohol is proportional to the square root of the change in intensity of light from a 1000 Watt lamp.

ETHYL ALCOHOL AND BROMINE.

This reaction has been studied by Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916)) and by Bhattacharya and Dhar (*Z. anorg. u. allg. Chem.* **176**, 372 (1928)), and the following results have been observed (see page 152).

Einstein's law of photochemical equivalence is not obeyed. Quantum yield increases with temperature and the frequency of the incident radiation.

The velocity of this reaction is proportional to the square root of the change in intensity of light from a 1000 Watt lamp.

N/113.7 bromine and 25% ethyl alcohol. 10 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient	Quantum Efficiency
Dark	20	0.00465	2.84	
	30	0.0132	2.77	
	40	0.0366		
Sunlight	20	0.110	1.54	195
	30	0.170	1.49	335
	40	0.254		545
$\lambda = 4725 \text{ \AA}$	20	0.00575	2.36	2.5
	30	0.0158	2.08	5.44
	40	0.0420		2.68
$\lambda = 5650 \text{ \AA}$	20	0.00646	2.04	3.5
	30	0.0169	2.02	8.1
	40	0.0441		19.4
$\lambda = 7304 \text{ \AA}$	20	0.00540	2.67	1.11
	30	0.01520	2.45	2.1
	40	0.0415		3.5

N/50 bromine and 10 c.c. propyl alcohol diluted to 100 c.c., 10 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient	Quantum Efficiency
Dark	20	0.0042	2.93	
	30	0.0126	2.84	
	40	0.0359		
Sunlight	20	0.0245	1.6	
	30	0.0450	1.4	
	40	0.0813		
$\lambda = 4725 \text{ \AA}$	20	0.00620	2.15	42
	30	0.0171	2.05	106
	40	0.0451		800
$\lambda = 5650 \text{ \AA}$	20	0.00720	2.13	49
	30	0.0190	2.0	110
	40	0.0487		690
$\lambda = 7304 \text{ \AA}$	20	0.00550	2.35	30
	30	0.0157	2.30	95
	40	0.0429		690

Berthoud and Béranek (*J. Chim. phys.* **25**, 28 (1928)) have also investigated this reaction, and have expressed its velocity by the following relation:

$$-\frac{d[\text{Br}_2]}{dt} = K \frac{I_0^{\frac{1}{2}} [\text{Br}_2]^{\frac{1}{2}} [\text{C}_2\text{H}_5\text{OH}]^m}{[\text{BrK}]^n}.$$

PROPYL ALCOHOL AND BROMINE.

The photochemical reaction between propyl alcohol and bromine has been investigated by Verma and Dhar (*Z. anorg. u. allg. Chem.* **184**, 58 (1929)). The experimental results are given on page 152.

The quantum yield increases with temperature and the frequency of the incident radiation. The relation between intensity and velocity varies from 1 to $\frac{1}{3}$ according to the velocities of the thermal and photochemical reactions.

ISOPROPYL ALCOHOL AND BROMINE.

Verma and Dhar (*loc. cit.*) investigated the photochemical reaction between isopropyl alcohol and bromine and obtained the following results:

N/50 bromine and 20 c.c. isopropyl alcohol diluted to 100 c.c., 20 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient	Quantum Efficiency
Dark	20	0.00240	2.96 2.80	
	30	0.00710		
	40	0.0199		
Sunlight	20	0.0290	1.28 1.27	
	30	0.0414		
	40	0.0640		
$\lambda = 4725 \text{ Å}$	20	0.00720	2.29 2.1	42
	30	0.0181		85
	40	0.0430		256
$\lambda = 5650 \text{ Å}$	20	0.00830	2.28 2.0	41
	30	0.0209		97
	40	0.0469		374
$\lambda = 7304 \text{ Å}$	20	0.00670	2.31 2.20	33
	30	0.0160		60
	40	0.0395		272

Einstein's law of photochemical equivalence is not followed. The quantum yield increases with temperature and the frequency of the incident radiation. The relation between intensity and velocity of this reaction varies from 1 to $\frac{1}{2}$ according to the velocities of the thermal and photochemical reactions.

BUTYL ALCOHOL AND BROMINE.

Verma and Dhar (*loc. cit.*) investigated the kinetics, quantum efficiency, and temperature coefficients of this reaction in sunlight, and in the three ranges of the visible spectrum. The following are the experimental results:

N/50 bromine, and 5 c.c. butyl alcohol diluted to 100 c.c.; 20 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient	Quantum Efficiency
Dark	20	0.0020		
	30	0.0056	2.8	
	40	0.0136	2.4	
Sunlight	20	0.0203		
	30	0.0299	1.17	
	40	0.0426	1.10	
$\lambda = 4725 \text{ \AA}$	20	0.0083		65
	30	0.0161	1.7	69
	40	0.0293	1.5	110
$\lambda = 5650 \text{ \AA}$	20	0.0124		83
	30	0.0222	1.6	77
	40	0.0368	1.4	136
$\lambda = 7304 \text{ \AA}$	20	0.00720		41
	30	0.0150	1.8	87
	40	0.0286	1.6	95

Einstein's law of photochemical equivalence is not obeyed. The relation between the intensity and velocity of this reaction varies from 1 to $\frac{1}{2}$ according to the velocities of the thermal and photochemical reactions.

The author is of the opinion that the atomization of a molecule of bromine need not always be the primary process in photochemical reactions with bromine as a reacting substance, because several wavelengths incapable of effecting the atomization of a bromine molecule have been found to be active in photobrominations. In these cases, activated bromine molecules appear to be the reacting units.

CHAPTER VIII.

Photochemical Reactions with Iodine as a Reacting Substance.

POTASSIUM OXALATE AND IODINE.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **16**, 1097 (1916); *J. Chem. Soc.* **111**, 707 (1917); **123**, 1856 (1923)), Mukerji and Dhar (*J. Phys. Chem.* **33**, 850 (1929)), and Bhattacharya and Dhar studied this photochemical reaction in detail, and obtained the following experimental results:

N/2.95 potassium oxalate and N/113.6 I₂ and N/29.35 KI.

Condition	Temperature in °C	$K_{\frac{1}{2}}$ Semimolecular	Temperature Coefficient	Quantum Efficiency
$\lambda = 4725 \text{ \AA}$	20	0.00489	3.01	18.6
	30	0.0147		40
	36	0.0271		74.8
$\lambda = 5650 \text{ \AA}$	20	0.00425	3.2	3.6
	30	0.0136		14.9
	36	0.0261		23.6
$\lambda = 7304 \text{ \AA}$	20	0.00368	3.56	3.7
	30	0.0131		7.5
	36	0.0256		7.4
$\lambda = 8500 \text{ \AA}$	20	0.00187	4.0	2.1
	30	0.00767	3.9	5.2
	40	0.0309		31
Dark	30	0.0000489 (K_1)	6.88	
	40	0.000336 (K_1)		

In the dark the temperature coefficient of the reaction is very high, and Dhar (*J. Chem. Soc.* **111**, 707 (1917); **123**, 1856 (1923)) obtained the value 7.2 between 25° and 40°, and in sunlight the value 2.68 between 26° and 36°.

Einstein's law of photochemical equivalence is not applicable to this reaction. The quantum yield increases with temperature and the

The velocities of this reaction are found to be proportional to the square roots of the intensities of the incident light from a 1000 Watt lamp

SODIUM TARTRATE AND IODINE.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916)) observed that this reaction is photosensitive. Bhattacharya and Dhar (*J. Indian Chem. Soc.* **6**, 147 (1929)) determined the kinetics, temperature coefficients, and energetics of this reaction in the dark, and in radiations of different wavelengths.

Sodium tartrate N/2.42 and iodine N/100 in N/34.3 KI; 10 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting dark " K_1 "	Quantum Efficiency
Dark	20	0.000378		
	30	0.000948	2.51	
	40	0.00236	2.49	
$\lambda = 4725 \text{ \AA}$	20	0.000554		11.4
	30	0.00132	2.11	13.7
	40	0.00295	2.0	17.9
$\lambda = 5650 \text{ \AA}$	20	0.000506		8.6
	30	0.00123	2.2	12.2
	40	0.00295	2.09	13.7
$\lambda = 7304 \text{ \AA}$	20	0.000451		4.2
	30	0.00113	2.26	7.1
	40	0.00272	2.18	9.6
$\lambda = 8500 \text{ \AA}$	20	0.0003945		3.1
	30	0.000987	2.36	5.2
	40	0.00245	2.30	7.9

Light Absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	0.04	0.07	0.19	0.21	0.50	0.61	0.89
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	1.08	1.5	2.75	4	Beyond scale	Total absorption	Total absorption

Quantum efficiency increases with temperature and the frequency of the incident radiation. There is appreciable absorption in the region $\lambda = 7000 \text{ \AA}$. Hence the acceleration of the reaction in the region $\lambda = 7304 \text{ \AA}$ is due to the absorption of the incident radiation.

The reaction between sodium tartrate and iodine is almost directly proportional to the change in intensity, the source of light being a 1000 Watt lamp.

SODIUM LACTATE AND IODINE.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916)) observed that this reaction is photosensitive. Bhattacharya and Dhar (*J. Indian. Chem. Soc.* **6**, 146 (1929)) have investigated the reaction more completely. The experimental results are as follows:

Sodium lactate N/4.69 and iodine N/100 in N/34.3 KI.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Quantum Efficiency
Dark	20	0.000720	2.49	
	30	0.00179	2.31	
	40	0.00414		
$\lambda = 4725 \text{ \AA}$	20	0.000942	2.02	9.23
	30	0.00224	1.91	12.14
	40	0.00500		16.37
$\lambda = 5650 \text{ \AA}$	20	0.000862	2.11	7.27
	30	0.00209	2.03	11.75
	40	0.00475		14.56
$\lambda = 7304 \text{ \AA}$	20	0.000797	2.21	3.97
	30	0.00196	2.06	6.52
	40	0.00449		8.38
$\lambda = 8500 \text{ \AA}$	20	0.000741	2.38	2.5
	30	0.00184	2.20	4.9
	40	0.00425		6.7

Light Absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	0.03	0.05	0.15	0.17	0.47	0.55	0.78
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	1.05	1.42	2.69	4.0	Beyond scale	Complete absorption	

This reaction is directly proportional to the change in the intensity of light, the source being a 1000 Watt lamp.

SODIUM MALONATE AND IODINE.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **24**, 974 (1916)) observed that this reaction is photosensitive. Bhattacharya and Dhar have investigated this reaction more completely, and obtained the following results:

Sodium malonate N/5·12 and iodine N/100 in N/34·3 KI.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark " K_1 "	Order	Quantum Efficiency
Dark	20	0·00227	2·21	Bimolecular	
	30	0·00503	2·16		
	40	0·0109			
N/10·24 Na-malonate	20	0·00119	2·1		
	30	0·00251	1·99		
	40	0·00500			
$\lambda = 4725 \text{ \AA}$	20	0·00349	1·85		14·6
	30	0·00729	1·80		17·3
	40	0·0149			19·8
$\lambda = 5650 \text{ \AA}$	20	0·00317	1·9		12·4
	30	0·00674	1·82		16·4
	40	0·0140			17·3
$\lambda = 7304 \text{ \AA}$	20	0·00287	2·0		9·8
	30	0·00623	1·92		12·4
	40	0·0132			13·6
$\lambda = 8500 \text{ \AA}$	20	0·00251	2·08		1·9
	30	0·00553	2·0		3·2
	40	0·0120			5·2

Light Absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	0·03	0·06	0·14	0·18	0·49	0·56	0·76
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	1·05	1·45	2·72	4	Beyond α	Complete absorption	

The reaction between sodium malonate and iodine was found proportional to the square root of the change in intensity. The source of light was a 1000 Watt lamp.

ACETONE AND IODINE IN PRESENCE OF HYDROCHLORIC ACID.

Dhar (*loc. cit.*) and Bhattacharya and Dhar (*Z. anorg. u. allg. Chem.* **176**, 378 (1928)) investigated the photochemical reaction between iodine and acetone, and the following are the experimental results obtained (see page 161).

This reaction is proportional to the square root of the change in intensity of light. The source of light was a 1000 Watt lamp.

49% acetone and N/50 iodine, and N/17.8 KI in presence of N/9.42 HCl.
 5 c.c. 10 c.c. 5 c.c.

Condition	Temperature in °C	K_0 Zeromolecular	Temperature Coefficient after deducting the dark " K_0 "	Order	Quantum Efficiency
Dark	21	0.0650	3.21	Monomolecular	
	31	0.209	3.0		
	41	0.629			
24.5% acetone	21	0.0336	3.15	Monomolecular	
	31	0.106	2.83		
	41	0.300			
Sunlight	21	0.119	1.77		32
	31	0.305	1.70		66
	41	0.792			98
24.5% acetone	21	0.0594	1.7		
	31	0.150	1.66		
	41	0.373			
$\lambda = 4725 \text{ \AA}$	21	0.0828	2.7		15.4
	31	0.257	2.65		33
	41	0.756			82
$\lambda = 5650 \text{ \AA}$	21	0.0760	2.82		8.5
	31	0.240	2.74		32
	41	0.714			58
$\lambda = 7304 \text{ \AA}$	21	0.0701	2.94		3.6
	31	0.224	2.87		11.2
	41	0.672			23.8

FERROUS SULPHATE AND IODINE.

Banerji and Dhar (*Z. anorg. Chem.* **134**, 174 (1924)) studied this photochemical reaction in the dark and in sunlight, and Mukerji and Dhar in three different ranges of visible spectrum, and the following are the experimental results (see page 162).

Bhattacharya and Dhar reinvestigated this reaction in the regions $\lambda = 7304 \text{ \AA}$ and $\lambda = 8500 \text{ \AA}$, using Nutting's spectrophotometer to determine the changes in the concentration of iodine. The results are as follows (see page 162 below).

Rideal and Williams (*J. Chem. Soc.* **127**, 259 (1925)) and Kistiakowsky (*J. Amer. Chem. Soc.* **49**, 976 (1927)) have investigated this reaction, but report that the reaction is unimolecular, whilst our results show that the rate of disappearance of iodine is semimolecular. Moreover, using unimolecular constants, they conclude that Einstein's law is

N/6.06 FeSO₄ and N/90.92 iodine in presence of N/3 H₂SO₄.

Condition	Temperature in °C	$K_{\frac{1}{2}}$ Semimolecular	Temperature Coef- ficient after deduct- ing the dark " $K_{\frac{1}{2}}$ " $K_{34.5}/K_{24.5}$	Quantum Efficiency
Dark	24.5	0.000373 (K_1)	2.92	
	30.0	0.000675 (K_1)		
	34.5	0.00100 (K_1)		
$\lambda = 4725 \text{ \AA}$	24.5	0.00658	2.61	18.64
	30	0.0111		28.4
	34.5	0.0174		127.5
$\lambda = 5650 \text{ \AA}$	24.5	0.00585	2.79	16.8
	30	0.00996		25.7
	34.5	0.0162		106
$\lambda = 7304 \text{ \AA}$	24.5	0.00358	2.85	8.34
	30	0.00903		14.2
	34.5	0.0128		52.7

valid for this reaction. Our experimental results carried on with radiations of different frequencies show that the Einstein law is inapplicable to this reaction.

The relation between the intensity of light and velocity varies from $\frac{3}{2}$ to $\frac{1}{2}$ depending upon the velocities of the thermal and photochemical reactions, which can be changed by using different concentrations of sulphuric acid and by changing the quality of the incident light.

N/10 FeSO₄ + N/100 iodine (Reading taken using Nutting's spectrophotometer after adding 2 c.c. H₂SO₄).

Condition	Temperature in °C	$K_{\frac{1}{2}}$ Semimolecular	Temperature Coef- ficient after deduct- ing the dark " $K_{\frac{1}{2}}$ "	Quantum Efficiency
Dark	30	0.00040 K_1	2.8	
	35	0.000675 K_1		
	40	0.00112 K_1		
$\lambda = 7304 \text{ \AA}$	30	0.00137	2.46	7.1
	35	0.00213		9.2
	40	0.00348		16.7
$\lambda = 8500 \text{ \AA}$	30	0.00915	2.63	4.6
	35	0.00149		6.8
	40	0.00239		12.4

SODIUM NITRITE AND IODINE.

Banerji and Dhar (*Z. anorg. u. allg. Chem.* **134**, 172 (1924)) and Mukerji and Dhar studied this photochemical reaction, but they determined the change in iodine concentration with sodium thio-sulphate. As there is a slight induced reaction between sodium nitrite and iodine in presence of sodium thiosulphate this method is not exact. Recently Bhattacharya and Dhar have reinvestigated this reaction more completely by determining the change of iodine concentration by Nutting's spectrophotometer, and the following are the results:

Sodium nitrite $\frac{2}{3}$ N (5 c.c.) and iodine N/32 (10 c.c.) and N/8.04 KI in presence of N/6.25 CH_3COONa (5 c.c.).

Condition	Temperature in °C	$K_{\frac{1}{2}}$ Semimolecular	Temperature Coefficient after deducting the dark " K_1 "	Total Order	Quantum Efficiency
Dark	30 40 50	0.00965 (K_1) 0.0259 (K_1) 0.0673 (K_1)	2.70 2.60	Bimolecular	
$\frac{1}{3}$ N NaNO ₂ dark	30	0.00490 (K_1)			
	30	0.0260			61
$\lambda = 4725 \text{ \AA}$	40 50	0.0529 0.103	2.0 1.91		190 210
	30	0.0228			36
$\lambda = 5650 \text{ \AA}$	40 50	0.0510 0.108	2.21 2.10		83 95
	30	0.0218			30
$\lambda = 7304 \text{ \AA}$	40 50	0.0506 0.112	2.29 2.19		64 73
	30	0.0147			18
$\lambda = 8500 \text{ \AA}$	40 50	0.0406 0.105	2.39 2.35		31 49

The relation between intensity and velocity varies from $\frac{3}{2}$ to $\frac{1}{3}$ depending upon the velocities of the thermal and photochemical reactions.

Berthoud and Berger (*J. Chim. phys.* **25**, 542 (1928)) have also investigated this reaction and have stated that the following processes take place in it:

- (1) $\text{I}_2 + h\nu = 2 \text{I}$; (2) $2 \text{I} + \text{H}_2\text{O} = \text{HIO} + \text{I}' + \text{H}'$;
- (3) $\text{HIO} + \text{I}' \rightarrow \text{I}_2 + \text{OH}'$; (4) $\text{HIO} + \text{NO}'_2 \rightarrow \text{NO}'_3 + \text{H}' + \text{I}'$;
- (5) $\text{I}_2 + \text{I}' \rightleftharpoons \text{I}_3$.

HYDROXYLAMINE HYDROCHLORIDE AND IODINE IN PRESENCE OF HYDROCHLORIC ACID.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **24**, 1097 (1916)) observed that this reaction is photosensitive. Bhattacharya and Dhar have now determined the kinetics, temperature coefficients, and energetics of this reaction in the dark, and in radiations of different wavelengths. The following are the experimental results:

Hydroxylamine hydrochloride N/5 (5 c.c.) iodine N/100 (10 c.c.) and N/17.8 KI, in presence of 1.25 N HCl (5 c.c.).

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Total Order	Quantum Efficiency
Dark	20 30 40	0.00534 0.0136 0.0335	2.54 2.46	Bimolecular	
N/2.5 Hydroxyl- amine hydro- chloride "dark"	20 30 40	0.0102 0.0270 0.0685	2.65 2.54		
$\lambda = 4725 \text{ \AA}$	20 30 40	0.00888 0.02045 0.0461	1.93 1.84		11.2 13.5 16.2
$\lambda = 5650 \text{ \AA}$	20 30 40	0.00753 0.0182 0.0427	2.1 2.0		8.3 12.1 15.2
$\lambda = 7304 \text{ \AA}$	20 30 40	0.00646 0.0161 0.0388	2.23 2.12		3.1 6.2 8.3
$\lambda = 8500 \text{ \AA}$	20 30 40	0.00592 0.0146 0.0362	2.28 2.23		2.35 3.8 5.6

The relation between velocity and intensity varies from 1 to $\frac{1}{3}$ depending upon the velocity of the thermal and photochemical reactions.

Light absorption:

Region in Å	7000	6707	5970	5870	5490	5320	5200	5000	4910
Extinction Coefficient	0.03	0.08	0.14	0.32	0.45	0.51	0.62	0.69	0.83
Region in Å	4800	4720	4670	4550	4400				
Extinction Coefficient	0.96	1.3	2.4	3.8	α				

HYDRAZINE HYDROCHLORIDE AND IODINE AND HYDROCHLORIC ACID.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **24**, 1097 (1916)) observed that this reaction is photosensitive. Bhattacharya and Dhar have now determined the kinetics, temperature coefficients, and energetics of this reaction in the dark, and in radiations of different wavelengths. The rate of reaction was determined by estimating the unchanged iodine by thiosulphate. The experimental results are as follows:

Hydrazine hydrochloride N/5 (5 c.c.) and iodine N/100 (10 c.c.) and N/17.8 KI in presence of 1.25 N HCl (5 c.c.).

Condition	Temperature in °C	K_1 Mono- molecular	Temperature Coefficient after deducting the dark " K_1 "	Total Order	Quantum Efficiency
Dark	25	0.00465	2.6	Bimolecular	
	35	0.0121	2.5		
	45	0.0302			
N/2.5 Hydrazine hydrochloride "dark"	25	0.00935	2.7		
	35	0.0252	2.6		
	45	0.0655			
$\lambda = 4725 \text{ \AA}$	25	0.00765	1.97		13.2
	35	0.0180	1.88		15.6
	45	0.0413			17.3
$\lambda = 5650 \text{ \AA}$	25	0.00673	2.07		11.1
	35	0.0164	1.98		12.3
	45	0.0387			14.7
$\lambda = 7304 \text{ \AA}$	25	0.00589	2.18		6.5
	35	0.0148	2.08		8.3
	45	0.0358			11.2
$\lambda = 8500 \text{ \AA}$	25	0.00523	2.24		2
	35	0.0134	2.15		3.8
	45	0.0330			4.9

Light absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	0.03	0.09	0.15	0.35	0.48	0.52	0.63
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	0.72	0.85	0.98	1.02	2.5	3.6	α

The relation between intensity and velocity varies from 1 to $\frac{1}{2}$ depending upon the velocities of the thermal and photochemical reactions.

The author is of the opinion that the atomisation of a molecule of iodine need not always be the primary process in photochemical reactions with iodine as a reacting substance, because radiations of several wavelengths, which are incapable of causing the atomisation of an iodine molecule, have been found to be active in photochemical reactions involving iodine. In these cases activated iodine molecules appear to be the reactive units.

CHAPTER IX.

Photochemical Reactions involving Oxygen as a Reacting Substance.

OXIDATION OF HYDROGEN IODIDE.

A great deal of experimental work has been carried out on the photochemical oxidation of HI in aqueous solutions, but the results obtained by different workers are discordant. Plotnikoff (*Z. physik. Chem.* **58**, 214 (1907)); **64**, 215 (1908) was the first to study this reaction systematically, although Lemoine (*Ann. de Chimie Phys.* **5**, 12, 240 (1877)) was the first to observe that the oxidation of acid solutions of KI, which proceeds at a measurable speed in the dark, is markedly accelerated by light of radiations near 4306 Å. Plotnikoff claimed that this narrow spectral region alone was photochemically active, and that the velocity of the reaction was proportional to the concentration of the dissolved oxygen and increased less rapidly than the iodide or hydrogen ion concentration. He assumed that the photochemical velocity was not influenced by the velocity of the simultaneous thermal oxidation. According to Plotnikoff the velocity of oxidation was directly proportional to the incident radiation.

Later on Strachoff (*Z. wiss. Phot.* **18**, 227 (1919)) studied the influence of iodine on the photochemical oxidation of HI; the iodine was used (1) as a separate light filter, and (2) in the reacting solution which was made 0.1 Normal with respect to KI and HCl. The following are the results of Strachoff:

$$\lambda = 4360 \text{ Å.}$$

1. Iodine as light filter (2 cms. layer):

I ₂ Millimols per litre	0.0	2.0	3.0	8.0	16	25.6
Velocity of reaction	120	105	80	60	16	8
						The velocity of dark reaction.

2. Iodine in the reacting solution (2.5 cms. layer):

I ₂ Millimols per litre	0.0	2.7	12.3	27.0	53.4	61.3	67.9	87.0
Velocity of reaction	120	120	120	119	80	72	60	50

The marked difference between these two sets of experiments indicates that I_3 ions have an accelerating influence on the velocity of the reaction, possibly due to photosensitization. Winther (*Kon. Danske, vid. Selsk. Mat. phys. Medd.* **2** Nos. 2 and 3 (1920)) supports the above view regarding the function of iodine, and concludes that solutions of HI free from iodine are not sensitive to light. Winther (*Z. physik. Chem.* **109**, 236 (1924)) thus attributes the photochemical oxidation of HI entirely to the primary absorption of light by I_3 ions. Consequently Winther worked with solutions of acidified KI containing definite amounts of iodine usually large enough to ensure a complete light absorption in the spectral region employed. The experiments carried out in radiation 3660 Å showed that the velocity of the reaction is proportional to the square root of the incident radiation at low light intensities (50—400 ergs per second); whereas at higher light intensities (780—1600 ergs per second) it passes through a maximum, and a doubling of the absorbed light energy beyond that point results in a 10% decrease of the velocity. Winther's results were partly different from those of Plotnikoff. Winther measured the absorbed light energy and obtained varying quantum yields, some of those found under the most favourable conditions, that is, low light intensity and high concentrations of the reactants, being more than 100 iodide ions oxidized per quantum. Under otherwise identical conditions, the yield was found to be more or less independent of the wavelength of the absorbed radiation, which varied in different experiments from 4360 to 2536 Å.

Stobbe and Steinberger (*Z. anorg. Chem.* **161**, 21 (1927)) have shown that if alkaline solutions of potassium iodide in vessels of quartz or uviol glass are exposed to sunlight or the light from a mercury vapour lamp, the alkalinity diminishes somewhat. It is concluded that the photolysis involves the reactions: $2 KI + O + H_2O = 2 KOH + I_2$; $KI + I_2 = KI_3$; $2 KOH + I_2 = KIO + KI + H_2O$; $3 KIO = KIO_3 + 2 KI$. With neutral iodine solutions, no free iodine is formed in absence of oxygen. The velocity of decomposition of iodide solutions in light increases with increase in the iodide concentration but is not directly related to it. If nuclei of iodine are already present at the outset, the velocity of reaction is greater at first than it is later; whilst if the nuclei are absent, the reverse is the case. The photolysis of neutral iodide solutions to which the oxygen of the air has access is a bimolecular reaction, but the velocity coefficient is dependent on the intensity and wavelength of the light. The wavelengths most active in bringing about decomposition are in the ultra-violet, but blue light has also a slight effect.

Recently Berthoud and Nicolet (*Helv. Chim. Acta* **10**, 475 (1927); *J. Chim. phys.* **25**, 163 (1928)) reinvestigated the photochemical oxidation of HI by O_2 . According to these investigators, two reactions proceed simultaneously in this case: (1) the direct oxidation of HI by O_2 and (2) the acceleration of the same reaction by iodine as a catalyst. The reaction is supposed to be sensitive to all the rays of the visible spectrum. Under the influence of red light, which is feebly absorbed and has been specially investigated, the velocity of the reaction increases as the square root of the iodine concentration and that of the light intensity. Berthoud and Nicolet state that the following equation expresses the velocity of the reaction:

$$\frac{d[I_2]}{dt} = KI_{0_{\text{absorbed}}}^{\frac{1}{2}} [I_2]^{\frac{1}{2}} [SO_4H_2]^{\frac{1}{2}} [KI]^x [O_2]^{0.9}$$

where x is a variable which increases with KI. The fact that the velocity is proportional to the square root of the absorbed light has been explained by Berthoud on the view that the primary process on illumination is the dissociation of iodine molecules into atoms. They assume that iodine atoms combine with oxygen forming an unstable compound (IO_2), which oxidises the iodide (I' , HI, and KI are possibly all involved). The following equations represent the various reactions:

- (1) $I_2 + h\nu = 2 I$,
- (2) $I + O_2 = IO_2$,
- (3) $IO_2 + 4 I' + 2 H_2O = 2 I_2 + I + 4 OH'$,
- (4) $IO_2 = I + O_2$,
- (5) $2 I = I_2$

The ions OH' which are formed in (3) combine immediately with the H' ions. From these processes Berthoud and Nicolet obtained an expression which is practically the same as that obtained empirically, for it agrees with the experimental results. In explaining the kinetic relations Winther advanced a theory in which he assumed that the I_3 ions, the primary cause of photochemical oxidation of HI, are activated upon quantized absorption of light energy, and that while they are still in the activated state they are capable of absorbing further energy quanta. Only those ions, however, which have absorbed one quantum can cause the photochemical reaction, whereas, by the absorption of subsequent quanta, they become deactivated in so far as their photochemical action is concerned. It is obvious that, qualitatively, this theory accounts for the decrease of the quantum yield

observed upon increasing the light intensity, since the change is thereby increased so that an activated I_3 ion before it can be consumed in the photochemical process may absorb a second light energy quantum. The actual mechanism of the photochemical reaction involves, according to Winther, the re-emission of a part of the absorbed radiation as fluorescence of short wavelength by each I_3 ion which has absorbed only one energy quantum, the absorption of this secondary radiation by the reactants O_2 etc., and eventually the renewed emission of light by the reactants. This theory of Winther seems doubtful in view of Stokes's rule of fluorescence, and very rarely the frequency of the fluorescent radiation (Anti-Stokes relation) is greater than that of the absorbed radiation. Furthermore, Winther's assumption of "Many quanta absorption" forces him to introduce extraordinarily large absorption coefficients and "life periods" of activated molecules, unsupported by experimental observations.

The experiments of Padoa and Miss Vita (*Chem. Zentr.* II, 524 (1928)) on the photo-oxidation of hydrogen iodide in air show that if the light is passed through a rotating sectored screen, the photochemical yield is at first increased with the number of alternations (transparent and dark) of the sectors, and then decreased to a constant value. Alternations, without dark sectors, of two or more colours caused greater dependence of yield on the velocity.

Recently Winther (*Z. physik. Chem. B*, **3**, 299 (1929)) has shown that in the oxidation of HI in the dark, the amount of iodine formed can be expressed by the relation, $\Delta t = kt + k_1 + tC_1$, where t is the time and C_1 is the iodine concentration. The oxidation in the dark thus consists of two reactions, one of which is proportional to the iodine concentration and the other independent of it. The second part of this reaction has been investigated, and the expression found for the total dark reaction is:

$$\Delta t = Kt + \frac{(a_1 \sqrt[3]{K m_1'^2})}{(b_1 + m_1' \sqrt[3]{m_1' m_1})}$$

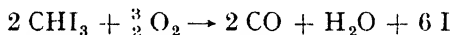
where a_1 , b_1 , and k are constants and m_1' and m_1 are the masses of iodine ions and total iodine present. A similar equation is obtained for the light reaction. According to Winther, it is possible to calculate, by certain simple assumptions, the velocity of the light reaction from that of the dark reaction by making use of quantitative absorption measurements.

So far we have discussed the action of light on acidified solutions of potassium iodide. Ross (*J. Amer. Chem. Soc.* **28**, 786 (1916)) and

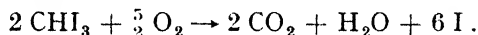
Kailan (*Monat. Chem.* **34**, 1209 (1913)) observed that ultra-violet light causes a slow decomposition of the neutral solutions of different salts of HI. No quantitative measurements, however, were undertaken in this case. Pinnow (*Ber.* **34**, 2528 (1901)), and others explained the influence of various foreign substances on the rate of reaction in acidified and neutral solutions of iodides. Under certain conditions of acidity, quinine and some dyes act as photosensitisers of the reaction, but the experimental evidence is not very conclusive.

OXIDATION OF IODOFORM.

Hardy and Willcock (*Proc. Roy. Soc.* **72**, 200 (1903); *Z. physik. Chem.* **47**, 347 (1904)) observed that solutions of iodoform in chloroform or benzene containing dissolved oxygen are oxidised to iodine by the action of light. They also confirmed the earlier observation that there is a photochemical after-effect in this reaction. Schoorl and van der Berg (*Ber. Deutsch. physik. Ges.* **385** (1905)) showed that in this photochemical oxidation two simultaneous reactions occur. About 80% of the iodoform is supposed to be oxidised according to the equation:



and 20% according to the equation:



Miss Bela Szilard (*Z. wiss. Phot.* **4**, 127 (1906)) came to the conclusion that the velocity of the photochemical oxidation of iodoform is approximately unimolecular, but that the decomposition seems incomplete, probably due to the retarding internal filter action of the iodine formed; and that by removing iodine the reaction is accelerated. The decay of the phenomenon of the photochemical after-effect is approximately unimolecular, and Miss Szilard compares it with the decrease of the activity of the enzymes. Plotnikoff (*Z. physik. Chem.* **75**, 337 (1910)) observed that the velocity of the decay of the photochemical after-effect was dependent on the concentration of iodoform in benzene, and that the temperature coefficient of this decay is 2.6, whilst the temperature coefficient of the photochemical oxidation of iodoform is 1.4. Plotnikoff (*Ibid.* **75** 385 (1910); **76**, 743 (1911)) investigated systematically the influence of different solvents on the photochemical oxidation of iodoform at 20° in presence of radiation 4360 Å.

The following are the results obtained by Plotnikoff:

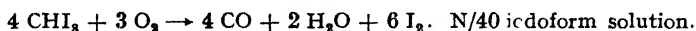
$$\text{CHI}_3 = 0.02 \text{ M.}$$

Solvent	Velocity constant	After-effect	E = Absorption coefficient of light	D = dielectric constant
CCl_4	39.4	2.4	23.4	2.2
C_6H_6	34.6	5.5	21.5	2.2
CS_2	24.1	—	45.9	2.6
$(\text{C}_2\text{H}_5)_2\text{O}$	16	—	10.9	4.3
	(rapid autocatalytic increase)			
$\text{CH}_3\text{COOC}_2\text{H}_5$	8.1	0.9	67.5	6.1
CH_3OH	3.2	—	66.4	31.0
	(decrease of constant)			
$\text{C}_2\text{H}_5\text{OH}$	2.5	—	10.2	26.0
CH_3COCH_3	0.7	—	53.0	21.5
$\text{C}_2\text{H}_5\text{OH} + 5\% \text{H}_2\text{O}$	1.4	—	—	—
$\text{C}_2\text{H}_5\text{OH} + 14.5\% \text{H}_2\text{O}$	0.7	—	—	—
$\text{C}_2\text{H}_5\text{OH} + 20\% \text{H}_2\text{O}$	0.5	—	9.7	33.5

The velocity constants in the second column were calculated by Plotnikoff on the assumption that the amount of iodine formed increases linearly with the time of illumination, and that the velocities of photochemical and of after reactions follow the additivity rule. The velocities of the photochemical reaction were therefore obtained by subtracting the rate of the after effect determined by special measurements from the total observed velocity. Plotnikoff concluded that the different velocities with which iodoform is oxidised in different solvents are not due to variations in the amount of light energy absorbed. Winther (*Trans. Faraday Soc.* **21**, 595 (1925)) pointed out that in Plotnikoff's experiments, the rate of iodoform oxidation generally decreases with the increase of the dielectric constant. A comparison between the velocity of iodine formation in Plotnikoff's experiments and the calculated amount of light energy absorbed indicates a quantum yield much greater than unity.

Comanducci and Meduri (*Gazz. Chim. ital.* **48**, 1, 238 (1918)) and Butler (*Chem. News* **125**, 38 (1922)) also studied this reaction, but did not measure the amount of energy absorbed. Recently Mukerji and Dhar (*J. Phys. Chem.* **33**, 850 (1929)) studied this reaction and determined the quantum yield, using different solvents in the total light from a 1000 Watt gas filled lamp. The results are recorded in the following table.

The oxidation takes place mainly according to the equation:



Condition	Temperature in °C	K_0 Zeromolecular	Temperature Coefficients K_{39}/K_{29}	Quantum Efficiency
Solvent: amyl	19	0.0111		3.4
alcohol	29	0.0130	1.15	3.54
1000 Watt lamp	39	0.0150		4.05
			K_{44}/K_{34}	
Solvent: Benzene	24	0.421		450
	34	0.496	1.05	480
1000 Watt lamp	44	0.521		530

The velocity of this reaction is directly proportional to the intensity of the incident light from a 1000 Watt lamp.

OXIDATION OF QUININE.

Weigert (*Nernst Festschrift*, Halle, 464 (1912)) observed that oxygen is absorbed by aqueous solutions of quinine under the action of violet and ultra-violet light from a mercury lamp, and that the quinine molecules are the light-absorbing component. The velocity of oxygen consumption is markedly retarded by hydrogen ions, and hydrochloric acid concentration of 0.1 N is sufficient to bring the reaction to a standstill. Oxygen is also a retarder, and the velocity of the reaction is almost inversely proportional to the oxygen concentration, but an optimum oxygen concentration must exist, since in its complete absence the rate of reaction is equal to zero. For a mixture of oxygen and nitrogen, containing 0.6 per cent oxygen, the velocity of oxidation is about 30 times as large as for pure oxygen. A similar influence of the oxygen concentration on the reaction velocity has also been observed in the photochemical oxidation of fluorescein and tetra-iodofluorescein. The reaction undoubtedly proceeds through the formation of stable intermediate products of peroxide character. This is evidenced by the earlier experiments of Iodlbauer and Tappeiner (*Münchener medizin. Wochenschr.* 1139 (1904)), who observed that previously illuminated quinine solutions can liberate iodine from an iodide. Weigert concluded that the intermediate product is not hydrogen peroxide but is associated with quinine molecules, and he could obtain as much as 42% of the chemically absorbed oxygen in the active state. Weigert observed that although the peroxide is stable in the dark at ordinary temperature, it

is decomposed by the action of radiation of the same wavelength as causes the oxidation of quinine. The quantum sensitivity of the quinine oxidation by free oxygen is very low in contrast to its oxidation by chromic acid. Bodenstein (*Z. physik. Chem.* **91**, 356 (1916)) estimated that, even under favourable conditions, as many as 200 light quanta are absorbed by quinine per reacting oxygen molecule.

OXIDATION OF SODIUM SULPHITE.

The thermal oxidation of sodium sulphite solutions has been the subject of numerous investigations by Bigelow (*Z. physik. Chem.* **26**, 493 (1898)), Titoff (*Ibid.* **45**, 641 (1903)), Dhar and co-workers (*Proc. K. Akad. Wetensch. Amsterdam* **23**, 299 (1920)), Moureu and Dufraisse (*Compt. rend.* **174**, 258 (1922); **175**, 127 (1922); **176**, 624, 797 (1923)), and others. There are numerous negative catalysts for this oxidation, and copper salts act as powerful accelerators. It has been observed that most of these negative catalysts are reducing agents. Dhar and collaborators found that the reaction is autocatalytic, and the temperature coefficient of the thermal reaction is about 2. Mathews and Dewey (*J. Phys. Chem.* **17**, 211 (1913)) observed that ultra-violet light markedly accelerates the reaction. Later Mathews and Weeks (*J. Amer. Chem. Soc.* **39**, 635 (1917)) reported that several organic substances retard the photochemical oxidation of sodium sulphite. Recently Mason and Mathews (*J. Phys. Chem.* **30**, 414 (1926)) showed that copper sulphate, which, according to Titoff, is a marked positive catalyst for the thermal reaction, retards the photochemical oxidation of sodium sulphite.

Bäckström (*J. Amer. Chem. Soc.* **49**, 1460 (1927); *Trans. Faraday Soc.* **24**, 601 (1928)) observed that as many as 50,000 molecules of sodium sulphite react per absorbed quantum of wavelength 2536 Å. According to Bäckström, alcohols affect the rates of photochemical and thermal reactions identically. Following Christiansen's theory (*J. Phys. Chem.* **28**, 145 (1924)), Bäckström interprets his results on the view that not only the photochemical but also the thermal oxidation of sodium sulphite is a chain reaction. The influence of negative catalysts is principally to reduce the length of the chains. Alyea and Bäckström (*J. Amer. Chem. Soc.* **51**, 90 (1929)) have shown that the chain length is the same for the thermal and the photochemical reactions, and is equal to the photochemical quantum efficiency. This may also be expressed by saying that in the light reaction the induced oxidation obeys the Einstein equivalence law. This is a

result which is completely analogous to the one obtained by Miss Cremer (*Z. physik. Chem.* **128**, 285 (1927)) in a study of the photochemical hydrogen-chlorine combination in the presence of oxygen. Here O_2 acts as an inhibitor, and the reaction is accompanied by an induced, or "photosensitized" formation of water. This induced reaction was found by Miss Cremer to be independent of the oxygen pressure and to obey the equivalence law, two molecules of water being formed for every light quantum absorbed by chlorine.

OXIDATION OF ALDEHYDES.

Bäckström (*loc. cit. Medd. Vet. Akad. Nobel Inst.* **6**, No. 15, No. 16 (1927)) showed that in the photochemical oxidations of benzaldehyde and heptaldehyde by oxygen, in radiations of wavelengths 3660—2536 Å, numerous molecules react per quantum of light energy absorbed, and these oxidations, like that of sodium sulphite, reveal chain mechanism. About 10,000 molecules of benzaldehyde vapour are oxidised per quantum of absorbed energy, the yield being nearly constant in the region 3660—2536 Å. The quantum yield of heptaldehyde oxidation increases from 7500 in light of wavelength 3130 Å to about 15,000 molecules per quantum in the light of wavelength 2536 Å.

Here, too, it was shown qualitatively that all substances which retard the photochemical rate of reaction act analogously in the thermal reaction. Quantitatively, however, the relations are not as simple as in the case of sulphite oxidation. Bäckström concludes from his experimental results that internal light filters, because they actually absorb ultra-violet radiation, which was used by him in his experiments, do not play an important rôle as inhibitors in the reaction mechanism. Bäckström observed that just as in the thermal oxidation of benzaldehyde and heptaldehyde, so also in their photochemical reaction with oxygen, the primary process is the formation of a per-acid molecule, which then reacts with another aldehyde molecule. The quantum yield of the per-acid formation was found to be very large; in fact so large that it is chiefly to the long chain reaction of this first stage that Bäckström attributes the chain character which he observed for the total oxidation. The secondary reaction of the per-acid with aldehyde, for instance: $C_6H_5COOOH + C_6H_5CHO = 2C_6H_5COOH$ is also light sensitive, but the quantum yield is much smaller and is of the order of 2 to 18 molecules per quantum absorbed. The velocity of the thermal reaction of the benzo-per-acid with benzaldehyde at 20° is unimolecular, and is half completed in 28 or 29 minutes.

Bäckström observed that the quantum yields of the formation and destruction of the per-acid are dependent on the light intensity; in other words, the velocity of the reaction is not directly proportional to the incident light intensity. We have emphasised the fact that the ratio of the velocity and intensity of one and the same reaction can vary from a proper fraction to 2 or more, depending on the acceleration of the photochemical reaction over the thermal reaction, and we are of the opinion that the oxidation of benzaldehyde is one of the same type as that discussed previously.

Bäckström showed that these oxidations can be photosensitized to the influence of longer waves by adding various light absorbing substances. Thus, for instance, diacetyl and benzil act as photosensitizers for the benzaldehyde oxidation; benzophenone, benzil, benzaldehyde etc. in the oxidation of heptaldehyde; sodium benzoate, acetone, potassium iodide, rhodamine B etc., in the oxidation of sodium sulphite solution.

The mechanism of these photosensitizations is probably not a direct transfer of energy during inelastic collisions. Bäckström suggests that the process by which the reaction chains are started in the photosensitized per-acid formation is probably a photochemical reaction between sensitizer and oxygen. Such a mechanism appears to be supported by the experiments of Noak (*Z. Botanik*, **12**, 273 (1920)), in which he showed that the oxidation of sodium sulphite can be photosensitized to visible light by means of eosin, fluorescein, and methylene blue, and that peroxides of the sensitizers are formed as intermediate products.

In explaining the mechanism of the reaction chains, Bäckström starts with the theory of Christiansen, and suggests that the "hot" molecules of the reaction products transfer their energy to the molecules of the reactant, causing them to be activated into quantum states, which lead to the absorption in the ultra-violet. His view is that the chain mechanism involved in the thermal and photochemical oxidation of benzaldehyde is similar to that in the photochemical hydrogen-chlorine reaction.

BLEACHING OF DYES IN COLLODION FILMS.

Originally Lasareff (*Ann. Physik* **24**, 661 (1907)) asserted that the rate of bleaching of different dyes in collodion films is determined solely by the amount of absorbed light energy, and is independent of

the wavelength of incident radiation. The measurements of the light energy showed that the amounts of energy required for the bleaching of different dyes exceeded even their heats of combustion. In the following table, the numbers of calories of radiant energy which cause the bleaching of one gram of dye under the influence of radiations of wavelengths 5400—6400 Å are recorded:

Chinaldincyanin	16,000 cal/gram.
Pinachrom	30,000 "
Cyanin	48,000 "
Lepidincyanin	58,000 "
Pinaverdol	117,000 "

These values indicate, as Bodenstein (*Ann. Physik* **37**, 812 (1912)) pointed out, that hundreds of light quanta must be absorbed in order to bleach one dye molecule.

Later on, Lasareff (*Ann. Physik* **37**, 812 (1912)) showed that the rates of bleaching of cyanin and of orthochrom in solid films of pure dye, and of pinacyanol in collodion films, are dependent on the wavelength of the absorbed radiation. Thus, the photochemical yield per calorie absorbed decreased for cyanin in the ratio 1 : 0.44 between the wavelengths 5430 and 6320 Å, for orthochrom in the ratio 1 : 0.71, and for pinacyanol in the ratio 1 : 0.39. According to Lasareff (*Z. physik. Chem.* **78**, 657 (1911); **98**, 94 (1921)), the bleaching is mainly due to the oxidation of the dye by oxygen. Besides the reaction due to the presence of oxygen in the films, light causes another chemical change manifested by decolorisation of the dye, and this proceeds unaltered even in a vacuum, but the chemical nature of this reaction is not understood. Apparently the nitrocellulose of the collodion takes part in the reaction. Schwezoff (*Z. wiss. Phot.* **9**, 65 (1910)) determined the temperature coefficient of the photochemical bleaching of these dyes in collodion films, and obtained values ranging from 1.04 to 1.08 for a 10° rise. In determining these temperature coefficients Schwezoff utilised the same amount of light energy absorbed at different temperatures.

Wawiloff (*Z. physik. Chem.* **100**, 266 (1922)) investigated the thermal bleaching of pinaverdol, cyanin, lepidincyanin, and chinaldincyanin between 60° and 120°, and this thermal bleaching appears to be entirely due to the catalytic influence of collodion, since pure solid dyes are stable in this temperature interval. The temperature coefficients of these thermal processes are of the order of 2 for a 10° rise.

Recently Weigert (*Z. Physik* **5**, 410 (1921)) and Predwoditeff and Netschajewa (*ibid.* **32**, 226 (1925)) observed that the initial rate of bleaching on illumination is proportional to the absorbed light energy only at very small dye concentrations in the collodion films. When the concentration of the dye is increased, the initial rate becomes a periodic function of the dye concentration. To explain this unusual behaviour, the authors suggest that the velocity of bleaching is not only dependent on the condition of each light absorbing molecule, but may also be influenced by the electric forces exercised by the adjacent dye molecules.

Zchodro (*J. Chim. phys.* **26**, 59 (1929)) has shown that the electric conductivity of collodion films coloured with cyanin, pinaverdol, or pinachrom increases on illumination with white light and monochromatic light, but that no increase is observed when the film has become decolorised. When illumination ceases, the electric conductivity gradually diminishes. The curves showing electric conductivity against wavelength resemble closely those obtained by Lasareff (*Ann. Physik* **24**, 661 (1907)) for the energy of light absorbed by these coloured films during decolorization, which is proportional to the energy of the light absorbed.

Zchodro (*J. Chim. phys.* **26**, 178 (1929)) has also measured the rates of decolorization of a solution of cyanin in benzene at 15°, 32° and 45°, and of gallocyanin in benzene at 14.8° and 43.5°. It appears from his results that in each case a rise in temperature retards the reaction. These results need confirmation.

OXIDATION OF NEOCYANIN.

Bhattacharya and Dhar (*J. Indian Chem. Soc.* **6**, 145 (1929)) have investigated the kinetics, energetics and temperature coefficients of the photochemical bleaching of neocyanin. Dilute solutions of neocyanin (Kodak) through which air was passed were exposed to light. The concentrations of the solutions were measured by the spectrophotometric method. The results are summarised in the following table (see p. 179).

Light absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	Complete absorption		Beyond α	1.96	0.86	0.44	0.21
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	0.24	0.27	0.31	0.43	0.48	0.54	0.62

It is interesting to note that the velocity of this reaction is greatest in the regions 7304 Å and 8500 Å where the light absorption is also maximum.

NEOCYANIN M/7-176.

The velocity of the reaction in the dark is negligible.

Region in Å	Temperature in °C	K_1 Monomolecular	Temperature Coefficient	Quantum Efficiency
$\lambda = 4725 \text{ Å}$	20	0.000641	1.29	2.5
	30	0.000830	1.20	3.6
	40	0.000990		4.7
$\lambda = 5650 \text{ Å}$	20	0.000830	1.2	1.8
	30	0.000990	1.11	2.7
	40	0.00110		3.9
$\lambda = 7304 \text{ Å}$	20	0.00102	1.12	1.1
	30	0.00114	1.05	2.1
	40	0.00120		3.1
$\lambda = 8500 \text{ Å}$	20	0.00112	1.1	0.98
	30	0.00123	1.04	1.65
	40	0.00128		2.30

The bleaching of neocyanin by air is proportional to the square root of the change in light intensity when the source of light is a 1000 Watt lamp.

OXIDATION OF DICYANIN.

The kinetics, energetics, and temperature coefficients of bleaching of dicyanin in light have been investigated by Mukerji and Dhar (*J. Phys. Chem.* 33, 850 (1929)). The velocity of the reaction was followed by measurements of the extinction coefficients spectrophotometrically. The following are the experimental results:

DICYANIN M/24,166.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark " K_1 " K_{40}/K_{30}	Quantum Efficiency
Dark	25	0.00099		
	30	0.00127	1.354	
	40	0.00172		

DICYANIN M/24,166 (Continued).

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark " K_1 " K_{40}/K_{30}	Quantum Efficiency
$\lambda = 4725 \text{ \AA}$	25	0.00337	1.099	0.258
	30	0.00379		0.207
	40	0.00450		0.33
$\lambda = 5650 \text{ \AA}$	25	0.00317	1.106	3.36
	30	0.00353		1.6
	40	0.00422		2.12
$\lambda = 7304 \text{ \AA}$	25	0.00309	1.056	0.29
	30	0.00340		0.66
	40	0.00397		0.89

The rate of the change is directly proportional to the intensity of the incident light. The source of light is a 1000 Watt lamp, the region being $\lambda = 5650 \text{ \AA}$.

CHAPTER X.

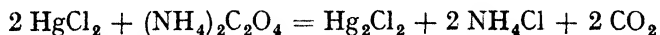
Other Photochemical Reactions involving Oxidation and Reduction.

Reduction of Mercuric Chloride by Organic Acids and their Salts.

MERCURIC CHLORIDE AND OXALATE.

The light sensitiveness of the mixture of mercuric chloride and ammonium oxalate was first discovered by Planché (*Jour. de. Pharm.* p. 49, (1815)). Becquerel and Frémy "La lumière, ses causes et ses effets" 1868, tome 2, p. 69) used a mixture containing 6.5 grams HgCl_2 and 12.5 grams oxalic acid dissolved in 100 c.c. water for the construction of a photometer. In an interesting work "Etude sur la force chimique continue dans la lumière du soleil" (1875), Marchand observed that the rate of decomposition of oxalic acid and mercuric chloride in presence of light is not regular.

Eder (*Wien. Akad. Ber.* 2 (1879)) made a thorough study of this photometer, and introduced some corrections which enabled it to be used in measuring accurately the chemical intensity of light. Eder studied the reaction between mercuric chloride and ammonium oxalate in sunlight. According to him, the reaction can be represented by the following equation:



There is an appreciable induction period in this reaction, which Eder ascribed to the time necessary for the solution to become saturated with the slightly soluble mercurous chloride. Eder considered this photochemical reaction to be a very convenient system for actinometric purposes. Subsequent investigations showed, however, that the reaction is very sensitive to several negative and positive catalysts, and hence not very suitable for an actinometer. Kastle and Beatty (*J. Amer. Chem. Soc.* 24, 182 (1900)) showed that the rate of mercurous chloride formation is accelerated by ferric and uranyl salts, and re-

tarded by chromic acid and chromates. Gros (*Z. physik. Chem.* **37**, 192 (1901)), and later Iodlbauer and Tappeiner (*Ber.* **38**, 2602 (1905)), stated that only fluorescent dyestuffs act as photosensitizers of the reaction, whereas those which do not fluoresce have practically no influence on the rate of mercurous chloride formation in sunlight. They also discovered that oxygen exerts a marked retarding influence on this photochemical reaction.

Winther (*Z. wiss. Phot.* **7**, 409 (1919); **8**, 197 (1910); **9**, 205 (1911)) studied the influence of various catalysts on this reaction, and showed that ferric salts accelerate the reaction only in small concentrations, whilst concentrated ferric chloride completely inhibits the photochemical reaction. The optimum concentration, which causes the formation of mercurous chloride to be 100 times more rapid than in a pure Eder's solution, is dependent on the concentration of oxygen dissolved in the mixture.

On the other hand, the retarding action of oxygen is dependent on the concentration of ferric salt, as will be seen in the following table:

FeCl ₃ in mols per litre	Relative rate of Hg ₂ Cl ₂ formation		
	Solution		
	free from oxygen	saturated with air	Ratio
2.8×10^{-4}	1000	158	6.3
2.8×10^{-5}	910	18	52.0
7×10^{-6}	400	4.4	90.0
0.0	160	0.16	1000

The decrease of retarding action of oxygen at higher concentrations of ferric salt is quite evident from the above table. Winther claimed that at higher concentrations of ferric chloride (10^{-2} N), oxygen accelerated the reaction. Since oxygen is used up during the course of this reaction, the rate of mercurous chloride formation plotted against time of illumination shows an autocatalytic increase in solutions originally saturated with oxygen. In oxygen-free solutions the order of the photochemical reaction is about two.

Winther reported that Eder's solution, when most carefully purified from iron salts, absorbs only light of wavelengths shorter than 3130 Å. On the other hand, the light sensitivity of a fairly pure solution begins at 5000 Å.

These observations led Winther to the conclusion that the sensitivity of longer waves is entirely due to minute quantities of ferric salts. In fact, Winther believed that even the short wavelengths absorbed by a pure Eder mixture do not react photochemically unless ferric salt is present in the solution. This view has not been confirmed

experimentally. Winther suggested that ferric oxalate is first reduced to ferrous oxalate in light, that this ferrous salt reduces mercuric chloride even in the dark at room temperature, that the kinetics of this change are complicated, and that it is retarded by oxygen. Hence Winther assumes that the primary action of light consists merely in the reduction of ferric oxalate, and that this reaction is independent of oxygen concentration. The formation of mercurous chloride is actually caused by a secondary and purely thermal reaction of ferrous ions, and this reaction is retarded by oxygen and exhibits other anomalies.

The function of H-ions in this solution has been overlooked by Winther, but Roloff (*Z. physik. Chem.* **13**, 327 (1894)) observed a strong retarding influence of H-ions on the photochemical decomposition of Eder mixture, and suggested that the reaction takes place between mercuric and oxalate ions.

Recently Berger (*Rec. trav. chim.* **40**, 387 (1921)) carried out a systematic study of the effect of electrolytes on the rate of mercurous chloride formation. Berger's results show that whereas the accelerating influence of ferric chloride is already noticeable at very small concentrations, the action of uranyl salts and of other nitrates is some 100 times less pronounced, although the general shape of the curve is unchanged. The ferric chloride curve of Berger is in marked disagreement with Winther's earlier results. Berger obtained only a threefold increase of the reaction velocity in presence of ferric chloride of $3 \times 10^{-3} \text{M}$ concentration, whilst Winther recorded a 100-fold acceleration. This discrepancy may be partly due to the fact that Winther used sunlight and glass vessels, whilst Berger had the total radiation from a lamp transmitted by quartz. Berger also pointed out that the view of Roloff that the reaction takes place between mercuric ions and oxalate ions is untenable, and accordingly suggested that the retardation of this reaction by electrolytes is due mainly to electrostatic forces of ionic charges, basing his considerations on the Debye theory of complete ionization (*Physik Z.* **24**, 185, 306 (1923)) and Brönsted's (*Z. physik. Chem.* **102**, 169 (1922)) view of ionic catalysis. Berger, however, entirely neglected the influence of iron salts and of oxygen in explaining the action of neutral salts.

Winther showed that the light sensitivity of Eder's solution can be shifted to longer wave regions in agreement with the absorption spectra of the dyes employed. Moreover, Winther and Oxholt-Howe (*Z. wiss. Phot.* **13**, 89 (1914)) showed that eosin used as photosensitizer is partly decomposed by light, and that the substances formed act as inhibitors of Eder's reaction.

Dhar (*J. Chem. Soc.* **111**, 707 (1917)) studied the kinetics of the reaction between $\text{K}_2\text{C}_2\text{O}_4$ and HgCl_2 in the dark at 79.8° and at 99.8° , using a glycerol thermostat. When the solutions are saturated with CO_2 no irregularities are observed, and the reaction is unimolecular with respect to both mercuric chloride and potassium oxalate, and hence the total reaction is bimolecular, although it is represented as $\text{K}_2\text{C}_2\text{O}_4 + 2 \text{HgCl}_2 = 2 \text{KCl} + \text{Hg}_2\text{Cl}_2 + 2 \text{CO}_2$. The dark reaction is extremely slow, and the temperature coefficient for a 10° rise between 80° and 100° is 2.36, whilst Eder working with sunlight obtained the value 1.19 for the photochemical reaction. Padoa and Miss Minganti (*Atti Accad. Lincei* **24**, 97 (1915)) showed that the temperature coefficient of Eder's reaction is a function of the wavelength of the incident radiation. The temperature coefficient increases from 1.05 in the wavelength region 2800—4000 Å to 1.21 in light of wavelength 4480 Å, and even to 1.75 when Eder's solution is sensitised to green light by tetrabromofluorescein. Dhar proved that the dark reaction is also induced by small quantities of oxidizing agents like HNO_2 , $\text{K}_2\text{S}_2\text{O}_8$, MnO_2 etc. He showed that the dark reaction between HgCl_2 and $\text{H}_2\text{C}_2\text{O}_4$ is induced by KMnO_4 , HNO_2 , etc. Very recently Roseveare and Olson (*J. Amer. Chem. Soc.* **51**, 1716 (1929)) have also studied the kinetics of the reaction between potassium oxalate and mercuric chloride in the dark.

Sanyal and Dhar (*Z. anorg. Chem.* **128**, 212 (1923)) determined the order of this reaction in sunlight, and the influence of different catalysts. The reaction appears to be zeromolecular with mercuric chloride, and unimolecular with ammonium oxalate in light. Salts of Fe^{++} , Fe^{+++} , Al^{+++} , Ni^{++} , Co^{++} , UO_2^{++} , Cr^{+++} , and MnSO_4 act as positive catalysts, whilst Cl_2 , Br_2 and Na_2SO_3 act as negative catalysts.

M/82 mercuric chloride, M/11.4 $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and M/15500 eosin.

Condition	Temperature in $^\circ\text{C}$	K_1 Monomolecular	Temperature Coefficient K_{40}/K_{30}	Quantum Efficiency
$\lambda = 5400 \text{ Å}$	26	0.00119	1.83	35.2
	36	0.00228		45.4
	46	0.00418		48
$\lambda = 4950 \text{ Å}$	26	0.00461	1.65	85.1
	36	0.00756		100.4
	46	0.0125		154
$\lambda = 4350 \text{ Å}$	26	0.00109	1.93	37.7
	36	0.00211		42.4
	46	0.00408		58

Mukerji and Dhar investigated the kinetics, temperature coefficients, and quantum yield of Eder's solution sensitized by eosin. The results are given in the table on p. 184.

The velocity of the reaction is proportional to the square root of the incident light intensity from a 1000 Watt lamp.

SODIUM FORMATE AND MERCURIC CHLORIDE IN PRESENCE OF SODIUM ACETATE.

The kinetics of this reaction have been studied in detail both in the dark and in the tropical sunlight by Dhar (loc. cit.).

The following experiments have been carried out by Mukerji and Dhar (*J. Phys. Chem.* **33**, 845 (1929)) in radiations of different wavelengths.

0.898 N. sodium formate, N/15 HgCl_2 and 0.2813 gram sodium acetate in 20 c.c. of the reacting mixture.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Quantum Efficiency
Dark	20	0.000662	4.52	—
	30	0.00299		
$\lambda = 4725 \text{ \AA}$	20	0.000985	2.66	1.2×10^2
	30	0.00385		6.5×10^2
$\lambda = 5650 \text{ \AA}$	20	0.00100	2.04	0.7×10^2
	30	0.00368		5.6×10^2
$\lambda = 7304 \text{ \AA}$	20	0.000808	4.11	0.273×10^3
	30	0.00359		0.68×10^3

The reaction is directly proportional to the intensity of the incident light from a 1000 Watt lamp.

Dhar (*Proc. K. Akad. Wetensch. Amsterdam* **18**, 1097 (1916)) also studied the reduction of mercuric chloride with other reducing agents in light. Thus mercurous chloride is formed when mixtures of mercuric chloride and reducing agents such as tartaric acid and sodium tartrate, citric acid and sodium citrate, lactic acid and sodium lactate, malic acid and sodium malate, malonic acid and sodium malonate, glycollic acid and sodium glycollate, mandelic acid, mucic acid, monochloroacetic acid, cane sugar, hydroxylamine hydrochloride, hydrazine hydrochloride, and ferrous sulphate are exposed to sunlight. The velocity of the photochemical reduction of mercuric chloride by an oxalate is very rapid in

comparison with that caused by the other reducing agents recorded above.

Winther (*Z. wiss. Photochem.* **11**, 60 (1912)) has investigated the reduction of mercuric chloride by ferrous chloride under different conditions. When the concentration of mercuric chloride is constant and is small, the velocity is approximately independent of the concentration of ferrous salt. The velocity appears to be maximum when the two salts are present in equimolar solutions. The presence or absence of oxygen is without appreciable influence on the equimolar solutions, but oxygen reduces the quantity of mercurous chloride obtained when a large excess of ferrous chloride is present. The most efficient rays are those of wavelength less than 2650 Å, as is shown by comparative experiments in quartz, uvial glass, and ordinary glass vessels.

REDUCTION OF FERRIC SALTS.

Eder (*Sitzb. Wien. Akad.* **82**, II, 606 (1880)) observed that sunlight causes the reduction of ferric salts when organic acids like oxalic, succinic, tartaric, citric, etc. are present in the solution. Lemoine (*Compt. rend.* **118**, 525 (1894)) made a detailed study of the photochemical reduction of ferric oxalate. Benrath (*Z. physik. Chem.* **74**, 115 (1910)) working with concentrated solutions found a reaction of zero order with several of these acids and ferric salts. It was also observed by Benrath (*Z. physik. Chem.* **74**, 115 (1910)) that ferric chloride is readily reduced to ferrous chloride by alcohols, glycerol, tartaric, citric, and oxalic acids, ether, etc. in light; if the solutions are concentrated enough, crystals of ferrous chloride separate out. Winther and Oxholt-Howe (*Z. wiss. Phot.* **74**, 196 (1914)) carried on extensive experiments with some organic acids and ferric salts (ferric oxalate, succinate, tartrate, citrate, and acetate), and observed that with wavelengths 4360 Å, 4050 Å, 3660 Å, 3130 Å the ensuing reaction velocity is of the zero order in solutions containing 0.1 M organic acid, and 0.006 to 0.0006 M FeCl_3 , and the reaction appeared to be autocatalytic. Measurements of quantum yield indicate that one ferric ion is reduced when one quantum is absorbed. The yields under otherwise identical conditions vary inversely as the light absorption coefficients of the solutions at different wavelengths. Thus, for example, the wavelength 4360 Å, which in all solutions is less strongly absorbed than the wavelength 4050 Å, causes a higher quantum yield. The observed deviations from Beer's absorption law undoubtedly support the view that there are several light absorbing compounds in these solutions of organic ferric

salts. The influence of the incident light increases with increasing dilution.

Padoa and Miss Vita (*Gazetta* **54**, 147 (1924)) have observed that the spectral region over which the photo-reduction of ferric chloride by oxalic acid takes place is somewhat limited; but the sum of the effects obtained in the blue and violet regions is 1.123 times that of white light. In the presence of a solution of quinine acid sulphate, the zone of the activating rays is widened, and the sum of the effects obtained in the blue, green, and violet lights is 2.125 times that of white light. These results appear doubtful and need confirmation. Miss Kornfeld [with E. Mencke] (*Z. Elektrochem.* **34**, 598 (1928)) has shown that the velocity of the reduction of ferric chloride by oxalic acid is proportional to the square root of the intensity of light in the blue, green, and violet, and is practically independent of the concentration of the reacting substances. Addition of ferrous sulphate retards the reaction at a rate proportional to the concentration of the added salt.

Recently Allmand and Webb (*J. Chem. Soc.* 1518, 1531 (1929)) have investigated the photolysis of potassium ferri-oxalate solutions, and have obtained the following values of quantum efficiency at different wavelengths:

Wavelength in Å	3130	3650	4050	4360
Quantum yield	1.59	1.16	0.91	0.89

They have drawn the following conclusions from their experimental results:

(1) The quantum yield is independent of the concentration of potassium ferri-oxalate between the limits 0.02 to 0.06 M.

(2) With 0.02 M solutions, the quantum yield is independent of the degree of decomposition between the limits 3.42 to 32.1%. It would appear, therefore, that the accumulation of ferrous oxalate does not retard the reaction apart from its internal light filter effect.

(3) For light of wavelength 3650 Å, containing a portion of 4050 Å, the quantum yield is independent of the intensity, whether continuous or intermittent, over a range of 15:1.

(4) If the absorbed active light be composed of varying proportions of two or more of the three mercury lines at 3650 Å, 4050 Å, and 4360 Å, then the degree of decomposition is about 30% higher than the additive effect of the different wavelengths.

(5) The decomposition of potassium ferri-oxalate, under the experimental conditions of Allmand and Webb, is proportional to the first power of the light intensity. The author is of the opinion that the

relation between light intensity and the velocity of this reaction is variable, like that in so many other reactions investigated.

IODIC ACID AND OXALIC ACID.

Banerji and Dhar (*Z. anorg. Chem.* **134**, 174 (1924)) have observed that this reaction is photosensitive. Bhattacharya and Dhar have now determined the kinetics, temperature coefficients, order, and energetics of this photochemical reaction in light from a 1000 Watt gas filled tungsten filament lamp.

The following are the experimental results:

Oxalic acid 2 N and iodic acid N/10, 10 c.c. each. There is no dark reaction.

Condition	Temperature in °C	K_0 Zeromolecular	Temperature Coefficients	Total Order	Quantum Efficiency
Light from 1000 Watt lamp	15	0.00244	1.72 1.70	Monomolecular	36
	25	0.00416			58
	35	0.00713			83
N/oxalic acid	15	0.00123	1.70 1.68	Monomolecular	19
	25	0.00209			26
	35	0.00352			47

The change in the iodine concentration was determined by a spectrophotometer.

POTASSIUM PERSULPHATE AND POTASSIUM IODIDE.

Price (*Z. physik. Chem.* **27**, 474 (1898)) observed that iodine is set free when potassium persulphate is added to potassium iodide in the dark. Dhar found that the reaction is photosensitive. Bhattacharya and Dhar (*Z. anorg. u. allg. Chem.* **176**, 374 (1928)) determined the kinetics, temperature coefficient, order, and energetics of this reaction in sunlight, and in light from a 1000 Watt lamp, using different combination of light filters. The following are the experimental results:

N/50 $K_2S_2O_8$ and N/5 KI, 10 c.c. each.

Condition	Temperature in °C	K_1 Mono- molecular	Temperature Coefficient after deducting the dark " K_1 "	Total Order	Quantum Efficiency
Dark N/2.5 KI	20	0.0215	1.95 1.90	2.5	
	30	0.0420			
	40	0.0799			

N/50 $K_2S_2O_8$ and N/5 KI, 10 c.c. each (Continued).

Condition	Temperature in °C	K_1 Mono- molecular	Temperature Coefficient after deducting the dark " K_1 "	Total Order	Quantum Efficiency
Dark N/5 KI	20	0.00758	1.90	Bi- mole- cular	
	30	0.0144	1.87		
	40	0.0270			
Sunlight N/2.5 KI	20	0.0548	1.3		
	30	0.0853	1.25		
	40	0.143			
Sunlight N/5 KI	20	0.0299	1.25		47
	30	0.0420	1.20		78
	40	0.0606			134
$\lambda = 4725 \text{ \AA}$ N/5 KI	20	0.0138	1.5		19.6
	30	0.0238	1.45		43
	40	0.0406			96
$\lambda = 5650 \text{ \AA}$ N/5 KI	20	0.0119	1.6		13.5
	30	0.0214	1.54		36
	40	0.0378			57
$\lambda = 7304 \text{ \AA}$ N/5 KI	20	0.00995	1.64		5
	30	0.0183	1.60		13.4
	40	0.0332			28.6

The liberation of iodine has been determined by a spectrophotometer.

The velocity of the reaction is directly proportional to the change in intensity. The source of light is a 1000 Watt lamp.

QUININE SULPHATE AND CHROMIC ACID AND SULPHURIC ACID.

This reaction was first studied by Goldberg (*Z. physik. Chem.* **41**, 1 (1902); *Z. wiss. Phot.* **4**, 56 (1906)) who observed the small value (1.02) for the temperature coefficient of this photochemical reaction, which was reinvestigated by Luther and Forbes under the action of the mercury lines 4060 Å and 3660 Å (using a uviol mercury lamp) (*J. Amer. Chem. Soc.* **31**, 770 (1909)). The velocity of the dark reaction was investigated by Dhar (*J. Chem. Soc.* **111**, 717 (1917)) who found the value 1.85 for the temperature coefficient of the dark reaction in presence of sulphuric acid.

The incident radiation is absorbed by both chromic acid and quinine sulphate. Now the light energy absorbed by a layer dx of the mixed solution of both substances is $-d I_{\text{abs}} = I (\alpha_1 C_1 + \alpha_2 C_2) dx$, where $\alpha_1, C_1; \alpha_2, C_2$ are respectively the light absorption coefficients and concentrations of the components. The fraction of light energy which is absorbed by quinine in the layer dx of the mixed solution is $-d I_{\text{abs quin.}} = I \alpha_1 C_1 dx$, and since the ratio

$$\frac{d I_{\text{abs quin.}}}{d I_{\text{abs}}} = \frac{\alpha_1 C_1}{\alpha_1 C_1 + \alpha_2 C_2} \quad (1)$$

is independent of the thickness of the layer, this equation gives directly the fraction of the total absorbed energy which is taken by quinine. Luther and Forbes measured the absorption coefficients (α) of both substances, and showed by applying equation (1) that the light absorbed by chromic acid is ineffective. The authors observed that the velocity of reaction was proportional to the amount of light energy absorbed by quinine, and was independent of chromic acid concentration, at least when this latter was varied from 0.012—0.001 N.

The photochemical reaction is assumed by Luther and Forbes to be exactly the difference between the total reaction in light and the dark reaction, and the combined effect of the velocities is additive. The experiments of Luther and Forbes seem to show that the velocity of the reaction is proportional to the absorbed energy, and independent of the frequency of the radiation.

Forbes and co-workers (*J. Amer. Chem. Soc.* **45**, 1891, (1923)) found that the rate of reaction is practically independent of the concentration of H_2SO_4 , if this is above 0.5 normal. The quantum yield of this reaction was not determined by these investigators, but was roughly calculated by Bodenstein (*Z. physik. Chem.* **85**, 329 (1913)). The quantum efficiency at different temperatures, and in radiations of different wavelengths, the influence of the intensity of the incident radiation and the change of concentration of sulphuric acid, and other aspects of this reaction, have been investigated by Mukerji and Dhar, and Bhattacharya and Dhar. Their results are as follows (see p. 191).

OXIDATION OF QUININE BY CHROMIC ACID.

The velocity of this reaction is proportional to the square of the intensity of the incident light from a 1000 Watt lamp. This relation has been varied from 2 to $\frac{1}{3}$ by changing the ratio of the thermal and photochemical reaction velocities by adding different amounts of sulphuric acid.

M/89 quinine sulphate in N/2 sulphuric acid, N/80-88 chromic acid in 1.31 N H_2SO_4

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficients after deducting the dark reaction K_{35}/K_{25}	Quantum Efficiency
$\lambda = 4725 \text{ \AA}$	25	0.000313	1.14	4.3
	30	0.000380		18.15
	35	0.000450		3
$\lambda = 5650 \text{ \AA}$	25	0.000258	1.39	4
	30	0.000325		2.66
	35	0.000400		1.53
$\lambda = 7304 \text{ \AA}$	25	0.000232	1.40	2.3
	30	0.000292		0.45
	35	0.000326		2.58
Dark	25	0.000204	1.60	
	30	0.000262		
	35	0.000326		

OXALIC ACID AND CHROMIC ACID.

Dhar (*J. Chem. Soc.* **111**, 707 (1917); **123**, 1856 (1923)) studied the kinetics and temperature coefficients of this reaction in the dark and in sunlight. Bhattacharya and Dhar (*Z. anorg. u. allg. Chem.* **176**, 377 (1928)) have determined the kinetics, temperature coefficients, and energetics of this reaction in light from a 1000 Watt gas filled tungsten filament lamp, using different combinations of light filters. The experimental results are as follows:

N/5 oxalic acid and N/111 chromic acid, 10 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Total Order	Quantum Efficiency
Dark N/5 $\text{H}_2\text{C}_2\text{O}_4$	20	0.00273	1.9	Tetra- mole- cular	
	30	0.00518	1.81		
	40	0.00938			
Dark N/10 $\text{H}_2\text{C}_2\text{O}_4$	20	0.000342	1.89		
	30	0.000649	1.81		
	40	0.00118			

N/5 oxalic acid and N/111 chromic acid, 10 c.c. each. (Continued).

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Total Order	Quantum Efficiency
$\lambda = 4725 \text{ \AA}$	20	0.00365	1.70		4.19
	30	0.00674	1.61		9.5
	40	0.0119			11.7
$\lambda = 5650 \text{ \AA}$	20	0.00380	1.65		5.1
	30	0.00695	1.60		7
	40	0.0122			9.3
$\lambda = 7304 \text{ \AA}$	20	0.00335	1.76		2.6
	30	0.00627	1.67		4.1
	40	0.0112			5

The velocity of this reaction is directly proportional to the change in intensity of the incident light from a 1000 Watt lamp.

TARTARIC ACID AND CHROMIC ACID.

Bhattacharya and Dhar have determined the kinetics, temperature coefficient, and energetics of this and two subsequent reactions in light from a 1000 Watt gas filled tungsten filament lamp, using different light filters:

Tartaric acid N/4.27 and chromic acid N/44.4, 10 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Quantum Efficiency
Dark	22	0.00143	2.13	
	32	0.00305	2.04	
	42	0.00621		
$\lambda = 4725 \text{ \AA}$	22	0.00174	1.9	8.8
	32	0.00364	1.86	12.7
	42	0.00731		15.6
$\lambda = 5650 \text{ \AA}$	22	0.00162	1.95	7.4
	32	0.00342	1.90	11.2
	42	0.00691		14.2
$\lambda = 7304 \text{ \AA}$	22	0.00154	2	5.6
	32	0.00327	1.95	8.3
	42	0.00664		11.0

Absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	0.03	0.10	0.14	0.16	0.18	0.24	0.27
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	0.48	0.54	0.61	0.67	0.83	0.95	1

The reaction between tartaric acid and chromic acid is proportional to the square root of the change in light intensity. The source of light is a 1000 Watt lamp.

CITRIC ACID AND CHROMIC ACID.

Citric acid N/6.75 and Chromic acid N/44.4, 10 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Quantum Efficiency
Dark	24	0.000359		
	34	0.00134	3.73	
	44	0.00485	3.65	---
$\lambda = 4725 \text{ Å}$	24	0.000610		3.6
	34	0.00191	2.59	6.7
	44	0.00645	2.46	8.2
$\lambda = 5650 \text{ Å}$	24	0.000570		2.7
	34	0.00188	2.66	4.8
	44	0.00622	2.54	6.2
$\lambda = 7304 \text{ Å}$	24	0.000487		1.5
	34	0.00171	2.89	4.2
	44	0.00587	2.75	5.2
$\lambda = 8500 \text{ Å}$	24	0.000413		1.1
	34	0.00151	3.15	3.2
	44	0.00534	2.90	4.3

Light absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	0.04	0.11	0.13	0.16	0.18	0.22	0.38
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	0.52	0.53	0.60	0.65	0.91	0.98	1.11

The reaction between citric acid and chromic acid is proportional to the square root of the change in light intensity. The source of light is a 1000 Watt lamp.

LACTIC ACID AND CHROMIC ACID.

N/4.72 lactic acid and N/44.4 chromic acid, 10 c.c. each.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting dark " K_1 "	Quantum Efficiency
Dark	22	0.00108	1.8	
	32	0.00195	1.75	
	42	0.00341		
$\lambda = 4725 \text{ \AA}$	22	0.00148		2.8
	32	0.00260	1.62	5.3
	42	0.00443	1.57	7.6
$\lambda = 5650 \text{ \AA}$	22	0.00136		2.4
	32	0.00243	1.70	4.6
	42	0.00419	1.63	5.9
$\lambda = 7304 \text{ \AA}$	22	0.00120		1.8
	32	0.00216	1.75	3.2
	42	0.00377	1.70	4.6

Absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction Coefficient	0.03	0.09	0.13	0.14	0.17	0.23	0.27
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction Coefficient	0.48	0.52	0.61	0.65	0.83	0.93	1

The reaction between lactic acid and chromic acid is directly proportional to the change in intensity of the incident light from a 1000 Watt lamp.

ALCOHOLS AND CHROMATE.

Plotnikoff (*Z. wiss. Phot.* **19**, 40 (1919)) has studied the photo-oxidation of ethyl alcohol of various concentrations by ammonium chromate and ammonium dichromate at 20° in light of wavelength 4360 Å. It has been observed that the velocity may be calculated by means of a linear equation, and that it is proportional to the concentration of alcohol. Increase in the concentration of the chromate or dichromate causes the reaction velocity to approach a maximum. The absorption coefficients of the mixtures have been measured, and are found to be a function of the alcohol concentration and to show a maximum. The dichromate follows Beer's

law, but chromate does not. The absorption changes brought out by the alcohol do not affect the reaction velocity. The velocities of the oxidation are the same with chromate as with dichromate. The temperature coefficient of the reaction is 1.02.

Bowen and Bunn (*J. Chem. Soc.* 2353 (1927)) have investigated the photochemical oxidation of methyl, ethyl, n-propyl, and isopropyl alcohols by potassium dichromate in radiations of wavelengths between 5000 and 3660 Å. The velocity of the reaction decreases regularly with decreasing acid concentration. In acid solution, aldehyde is formed without the production of any precipitate. In neutral and alkaline solutions the chromate ion is photo-chemically insensitive towards alcohols, and in neutral solution a precipitate of uncertain composition is formed. Bowen and Bunn have stated that the quantum yield is independent of the light intensity over a range of 1 : 80. These results are not in agreement with those obtained by Dhar and collaborators with chromic acid and other reducing agents, and should be confirmed.

Recently Bowen and Yarnold (*J. Chem. Soc.* 1648 (1929)) have concluded that of the ions $\text{HCr}_2\text{O}_7'$, $\text{Cr}_2\text{O}_7''$ and HCrO_4' present in a solution of chromic acid, only the first is photoactive, and then only when it has one or more alcohol molecules attached to it. In strong alcohol solutions, the quantum yield is approximately unity; in weaker solutions it is diminished owing to the presence of non-alcoholated $\text{HCr}_2\text{O}_7'$ ions, and of $\text{Cr}_2\text{O}_7''$ ions, which by absorbing light act as internal filters. With glycerol and chromic acid the quantum yield does not exceed 0.5.

Riesenfeld and Hecht (*Z. wiss. Phot.* 26, 369 (1929)) have investigated the photochemical reaction between sodium dichromate and ethylene glycol. It has been observed that water retards this photochemical reaction.

Morton (*J. Phys. Chem.* 33, 1135 (1929)) has drawn the following conclusions from his experiments on the photochemical oxidation of ethyl alcohol by potassium dichromate: (1) Under suitable conditions, the dichromate is the photosensitive substance, (2) with increasing acidity the dark reaction increases and the apparent action of light decreases, and (3) the light reaction can be varied from approximately zero to totality by varying the concentration of sulphuric acid. The results are not exactly in accordance with those of Luther and Forbes.

OXIDATION OF OXALIC ACID BY POTASSIUM PERMANGANATE.

The temperature coefficient of this reaction (Harcourt and Esson's reaction) has been determined in the dark (Purkayastha and Dhar, *Z. anorg. Chem.* **121**, 1561 (1922), and Banerji and Dhar, *ibid.*, **134**, 172 (1924)); as well as in sunlight (Dhar, *J. Chem. Soc.* **123**, 1857 (1923)). Mukerji and Dhar have determined the kinetics, temperature coefficient, and energetics of this reaction in light from a 1000 Watt lamp using different light filters.

$N/421.3 \text{ KMnO}_4$; $N/19.12 \text{ H}_2\text{C}_2\text{O}_4$; $N/337 \text{ MnSO}_4$ and $N/2.78 \text{ H}_2\text{SO}_4$.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark " K_1 " $\frac{K_1^{24.5}}{K_1^{14.5}}$	Quantum Efficiency
Dark	8.5	0.0220	3.09	
	14.5	0.0466		
	24.5	0.1440		
$\lambda = 4725 \text{ \AA}$	8.5	0.0429	2.78	93.8
	14.5	0.0865		133.0
	24.5	0.2550		245.0
$\lambda = 5650 \text{ \AA}$	8.5	0.0386	2.05	38
	14.5	0.0741		89
	24.5	0.2003		71
$\lambda = 7304 \text{ \AA}$	8.5	0.0351	2.4	39
	14.5	0.0652		36
	24.5	0.1886		36

The velocity of this reaction increases appreciably with the increase in the intensity of the incident light, but there is no simple ratio between the two. The region used is $\lambda = 4725 \text{ \AA}$.

OXIDATION OF LACTIC ACID BY POTASSIUM PERMANGANATE.

Bhattacharya and Dhar (*Z. anorg. u. allg. Chem.* **176**, 378 (1928)) have studied the kinetics, temperature coefficients, energetics, and order of this and the two subsequent reactions in light from a 1000 Watt gas filled tungsten filament lamp using different filters:

N/5.36 tartaric acid and N/98.45 KMnO_4 in presence of N/69 MnSO_4 .
 5 c.c. 10 c.c. 5 c.c.
 (Continued).

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Quantum Efficiency
$\lambda = 5650 \text{ \AA}$	16	0.0205		23
	26	0.0482	2.1	38
	36	0.110	2.0	63
$\lambda = 7304 \text{ \AA}$	16	0.0188		11
	26	0.0455	2.3	26
	36	0.107	2.2	37

The velocity of this reaction is proportional to the square root of the change in intensity of the incident light from a 1000 Watt lamp.

OXIDATION OF CITRIC ACID BY POTASSIUM PERMANGANATE.

The changes in the concentration of KMnO_4 were determined by a Nutting spectrophotometer.

N/5 citric acid and N/50 KMnO_4 in presence of N/69 MnSO_4
 5 c.c. 10 c.c. 5 c.c.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction K_{25}/K_{15}	Quantum Efficiency
N/5 Citric acid Dark	15	0.00473		
	25	0.0138	2.92	
	30	0.0219		
N/10 Citric acid Dark	15	0.00241		
	25	0.00675	2.80	
	30	0.0108		

It is a bimolecular reaction in the dark

$\lambda = 4725 \text{ \AA}$	15	0.00743		5.14
	25	0.0198	2.2	8.62
	30	0.0286		10.13
$\lambda = 5650 \text{ \AA}$	15	0.00681		4.14
	25	0.0186	2.3	6.32
	30	0.0273		8.45

N/5 citric acid and N/50 KNO_3 in presence of N/69 MnSO_4
 5 c.c. 10 c.c. 5 c.c.

It is a bimolecular reaction in the dark (Continued).

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction K_{25}/K_{15}	Quantum Efficiency
$\lambda = 7304 \text{ \AA}$	15	0.00609	2.35	3.12
	25	0.0170		5.35
	30	0.0259		7.21
$\lambda = 8500 \text{ \AA}$	15	0.00512	2.56	1.02
	25	0.0148		3.13
	30	0.0232		4.25

The velocity of this photochemical reaction is proportional to the square root of the change in intensity of the incident light from a 1000 Watt gas filled tungsten filament lamp.

CHAPTER XI.

Photochemical Decompositions.

DECOMPOSITION OF OZONE.

The thermal decomposition of ozone has been studied by numerous workers under different conditions. According to Warburg (*Ann. Physik.* **9**, 1286 (1903)), Clement (*ibid.* **14**, 334 (1904)), and Chapman and Jones (*J. Chem. Soc.* **97**, 2463 (1910)), the reaction is a bimolecular one having a temperature coefficient of 2.5 for 10° rise:



Jahn (*Z. anorg. Chem.* **48**, 260 (1906)), and Perman and Greaves (*Proc. Roy. Soc.* **80**, 353 (1908)) observed, however, that the velocity of the thermal decomposition is retarded by oxygen. Recently Griffith and McKeown (*Trans. Faraday Soc.* **21**, 597 (1925)) observed that the presence of hydrogen markedly accelerated the velocities of the thermal and photochemical reactions. Similarly helium, argon, and nitrogen also exert an accelerating influence.

Stark (*Ann. Physik.* **43**, 319 (1914)) and Stuchtey (*Z. wiss. Phot.* **19**, 161 (1920)) have shown that the chemiluminescence of ozone decomposition consists of numerous well defined bands extending from the visible to the far ultra-violet region, in fact even up to 2500 Å, which corresponds to 115,000 cal. According to Jahn (*Z. anorg. Chem.* **60**, 337 (1908)) the heat of bimolecular thermal decomposition of ozone is approximately 64,000 calories, which even together with the activation energy of 26,000 calories (corresponding to the temperature coefficient of 2.5 for a 10° rise) cannot account for the emission of these short wave radiations. It thus becomes necessary to assume that the mechanism of ozone decomposition involves a transfer of energy from the reaction products to the reacting molecules, and that accumulation of energy takes place (compare Wulf, *Proc. Nat. Acad. Sciences* **12**, 179 (1926)). The same conclusion could be drawn from the experiments of Smyth (*Proc. Nat. Acad. Sciences* **11**, 679 (1926)) on inelastic collisions between slow moving electrons and decomposing ozone molecules. He observed that collisions of the second type take place in this case,

whereby the energy of the active ozone molecules is transformed into the kinetic energy of the electrons. In the electron velocity distribution curve, Smyth obtained three maxima at 0.52, 1.75 and 4.3 volts, corresponding to 12,000, 40,000 and 111,000 calories respectively.

The photochemical decomposition of ozone has been extensively investigated. Regener (*Ann. Physik.* **20**, 1033 (1906)), and later Weigert (*Z. physik. Chem.* **80**, 78 (1912)), using ultra-violet radiations, found that the velocity of this decomposition per unit energy absorbed increased with increasing concentration of ozone. Miss Bahr (*Ann. Physik.* **33**, 589 (1910)) reported that the velocity of the decomposition was proportional to the amount of energy absorbed when the concentration of ozone was small. Warburg (*Sitzb. Preuss. Akad.* **644** (1913)) studied the decomposition of ozone in radiation of wavelength 2530 Å, and obtained the quantum yield 0.28 in mixtures of oxygen and ozone at atmospheric pressure. Ozone mixed with nitrogen or helium was found to decompose more rapidly; the quantum yield in nitrogen was 1.1 and in helium 1.7. At higher partial pressures of the latter, the quantum efficiency increased approximately as the square root of the ozone concentration and was influenced by the intensity of the light. Moisture decreased the velocity of decomposition. Warburg showed that since radiation of the wavelength 2530 Å is very strongly absorbed by ozone, the region where the photochemical reaction takes place at higher ozone concentrations is apparently limited to a thin layer of the gas. Moreover, under these conditions, the quantum yield is dependent on the ozone concentration.

According to Fabry and Buisson (*Compt. rend.* **156**, 782 (1913)), ozone shows marked selective absorption with a maximum at 2470 Å, 2480 Å. Ladenburg and Lehmann (*Ann. Physik.* **21**, 305 (1906)) showed that ozone possesses strong continuous absorption of radiations shorter than 3000 Å. Moreover, it possesses several absorption bands in the region 3000 Å to 3600 Å, and a group of bands in the visible part of the spectrum, particularly in the region 5000 Å to 6500 Å. In the infra-red ozone also possesses an absorption maximum near 6300 Å and longer wavelengths. It was generally assumed that ozone was stable towards visible light. Investigations of Griffith and Shutt (*J. Chem. Soc.* **119**, 1948 (1921)), initiated as a result of calculations made by Lewis in 1918 on the basis of the radiation theory of chemical action, have shown that ozone may be decomposed by radiations of wavelengths longer than 6700 Å, which lie in the red region of the visible spectrum. This prediction by Lewis, and subsequent confirmation by Griffith and Shutt, constitutes one of the important experimental

verifications of the radiation theory. Griffith and McWillie (*J. Chem. Soc.* **123**, 2767 (1923)) observed that the decomposition of ozone diluted with oxygen at atmospheric pressure is proportional to $(O_3)^{\frac{3}{2}}$. These authors confirm the earlier observations of Warburg that in visible light also the quantum yield increases with the increase of ozone concentration, and that the influence of foreign gases is in the following order:



Stern and Volmer (*Z. wiss. Phot.* **19**, 275 (1920)), in discussing Warburg's experiments, suggested that the primary action of light consisted in the formation of activated ozone molecules, and that these lost part of their energy by collision with oxygen molecules before they had a chance to react. In nitrogen and helium the yield of these inelastic collisions is smaller, and therefore the velocity of decomposition is faster. Griffith and McWillie suggested the same explanation of the acceleration of ozone decomposition by the presence of foreign gases, and this explanation seems to have been confirmed by the experiments of Kistiakowsky (*Z. physik. Chem.* **117**, 337 (1925)), who studied the reaction in radiation of wavelength 6200 Å with gas mixtures containing 70% ozone. The total pressure was varied from atmospheric to about 9 mm. The results obtained by Kistiakowsky are complicated. At high pressures the rate of ozone decomposition is represented by the equation:

$$-\frac{d[O_3]}{dt} = K_1 I_{\text{abs}} \sqrt{\frac{[O_3]}{[O_2]}}$$

At low pressures this equation is not in accord with the experimental results, the velocity of the reaction being only slightly retarded by oxygen, and almost independent of ozone concentration. The quantum yield in visible light is about one-tenth of that found by Warburg in 2530 Å. It will be interesting to note in this connection that Hibben (*Proc. Nat. Acad. Sci.* **13**, 626 (1927)) observed that ozone is stable towards infra-red radiations, which are absorbed by ozone. The exact mechanism of the photochemical decomposition of ozone remains unknown.

The temperature coefficient of ozone decomposition in ultra-violet light was found by Weigert (*Z. physik. Chem.* **80**, 78 (1912)) to be 1.15; Griffith and McKeown (*Trans. Farad. Soc.* **21**, 525 (1925)) obtained the value 1.34 in visible light. Bodenstein and Kistiakowsky found nearly the same value at high pressures, but at low pressures, where the velocity of the reaction is almost independent of the concentration of

ozone and where the quantum yield approaches 2, the temperature coefficient is about unity.

Weigert and Böhm (*Z. physik. Chem.* **90**, 189 (1916)) observed the formation of water when ozone and hydrogen are illuminated by ultra-violet light. Griffith and Shutt (*J. Chem. Soc.* **123**, 2752 (1923)) obtained similar results in visible light. Griffith and McWillie observed the formation of CO_2 when ozone and CO were exposed to visible light. The action of carbon monoxide differs from that of hydrogen in that the rate of ozone decomposition is only slightly accelerated by the presence of CO. The photosensitization of the decomposition of ozone by chlorine, first observed by Weigert (*Ann. Physik.* **24**, 243 (1907)), will be discussed elsewhere. Recently Bodenstein, Hartek, and Padelt (*Z. anorg. Chem.* **147**, 233 (1925)) observed that red light causes a rapid formation of chlorine hexoxide Cl_2O_6 when a mixture of ozone and chlorine are exposed to red light, which is absorbed mainly by ozone. The kinetics of this reaction appear to be complicated.

DECOMPOSITION OF HYDROGEN PEROXIDE.

Tian (*Compt. rend.* **151**, 1040 (1910); **156**, 1601, 1758, 1879 (1913)) studied the kinetics of the decomposition of H_2O_2 under the total radiation from a mercury lamp, and obtained a unimolecular velocity constant when the concentrations of hydrogen peroxide were small. He concluded that the rate of decomposition, instead of being proportional to the absorbed light energy, decreased with decrease of hydrogen peroxide concentration. Henri and Wurmser (*ibid.* **156**, 1012 (1913)) observed that the quantum yield in total radiation from a high tension spark discharge is about 100 molecules of H_2O_2 per quantum of light absorbed. Later on these authors, working with monochromatic radiations, obtained the following values of quantum yield with different wavelengths:

Concentration of $\text{H}_2\text{O}_2 = 0.037 \text{ N.}$				
Wavelength	2800	2558	2300	2100 Å
Light energy absorbed per decomposing molecule	1.54	1.55	1.49	1.61
Quantum yield	4.4	4.9	5.7	5.9

Henri and Wurmser concluded from their measurements that it is not the number of quanta, but the amount of absorbed light energy independent of wavelength, which controls the velocity of the reaction.

By varying the intensity they showed that a direct proportionality exists between the intensity and the velocity of the reaction. Recently Miss Kornfeld (*Z. wiss. Phot.* **21**, 66 (1921)) confirmed Tian's statement that the velocity decreases with decrease of concentration of hydrogen peroxide. Miss Kornfeld obtained the quantum yield 80 with 0.5 N neutral solution of H_2O_2 , and 24 with 0.016 N solution in monochromatic radiation of wavelength 3110 Å. Recently Winther (*Trans. Farad. Soc.* **21**, 45 (1925)) attempted to explain the differences in the quantum yield obtained by different authors, and suggested that the velocity of H_2O_2 decomposition is not proportional to the incident light intensity, and that since different investigators used different light intensities, they did not obtain concordant results. The following values of temperature coefficients for the photo-decomposition were obtained by different investigators:

	Temp. coeff.
Anderson and Taylor (<i>J. Amer. Chem. Soc.</i> 45 , 650, 1210 (1923))	1.43
Mathews and Curtis (<i>J. physik. Chem.</i> 18 , 166, 521 (1914))	1.50
Miss Kornfeld	1.32
Tian	1.15

It has been already emphasized that the greater the acceleration of a reaction by light, the smaller is the value of the temperature coefficient. In Tian's experiments the decomposition of H_2O_2 was most markedly accelerated, whilst in Mathews and Curtis's results the reaction was least accelerated, and hence the temperature coefficient was least in Tian's work and greatest in Mathews and Curtis's experiments.

Henri and Wurmser observed that hydrogen peroxide solutions show increasing absorption of radiations of wavelengths shorter than 3000 Å.

Rosanoff (*J. Russ. Phys. Chem. Soc.* **44**, 1146 (1912)) and Henri and Wurmser (*Compt. rend.* **156**, 1012 (1913); **157**, 126, 284 (1913)) have measured the ultra-violet absorption spectrum of hydrogen peroxide and their results are as follows:

Molecular extinction coefficient	0.422	3.0	20.0	75.0	127.0	127.0
Wavelength in Å.....	3110	2800	2540	2300	2100	2060

Recently Urey, Dawsey, and Rice (*J. Amer. Chem.* **51**, 1371 (1929)) have shown that the absorption spectrum of hydrogen peroxide vapour in the ultra-violet is continuous, with no indication of any structure, beginning at about 3000—3100 Å. They have also measured the absorption coefficients of a solution of hydrogen peroxide for wavelengths

from 3750 to 2150 Å, and those of its vapour for wavelengths 2150 to 2750 Å. The two absorption curves between 2150 to 2750 Å appear to be identical.

In a recent communication read before the Chemical Society, London, Allmand and Style (compare *J. Soc. Chem. Ind.* **49**, 144 (1930)) have come to the following conclusions regarding the photolysis of hydrogen peroxide: (1) The velocity varies as the square root of the light intensity; (2) the velocity diminishes with increase in concentration of H_2O_2 ; (3) the quantum efficiency diminishes with increase in the frequency of the light; (4) the thermal and photochemical reactions are similar; and (5) the decomposition has very long reaction chains. The conclusions (1) and (3) are not in accord with previous work on this most sensitive and complicated reaction.

Miss Kornfeld suggested that the light sensitive component in the decomposition is the hydrogen peroxide molecule, and that the primary action of light consists in breaking it up into an OH ion, an energy-rich H ion, and an oxygen atom. This latter then causes the decomposition of a varying number of other hydrogen peroxide molecules.

The inhibition of the decomposition of hydrogen peroxide has been investigated by several workers. Henri and Wurmser (*Compt. rend.* **157**, 284 (1913)) reported that in the presence of inorganic acids and alkalis the rate of photochemical decomposition is markedly retarded. Catalytic poisons, like H_2S , HCN etc., were more powerful inhibitors. Mathews and Curtis discovered several inhibitors, and noted that the influence of inhibitors on the velocities of thermal and photochemical reactions is in general different. Miss Kornfeld showed that the retarding influence of sulphuric acid is not due to a change of light absorption by H_2O_2 ; she observed smaller quantum yields in presence of this acid. Since sodium sulphate was found to be completely ineffective, she assumed that the hydrogen ion must be the retarding agent. Anderson and Taylor showed that the inhibiting action of several organic substances is largely due to the absorption of active radiation by these organic substances. These authors believe that the action of organic acids, esters, amides, and of quinine are satisfactorily accounted for on the view of light-screening action of these compounds, but report that in the case of alcohols and amines, no such simple relation between absorption spectra and their activity could be found. The influence of alkalis was observed to be 25 times greater than that of acids. Of neutral salts, only chlorides, and less strongly bromides, show retarding influence. The inhibiting action of acids and alkalis is markedly reduced by the

addition of neutral salts with a common ion, and hence the above authors concluded that H and OH ions are the effective agents, and that the retarding influence was practically independent of temperature.

Anderson and Taylor pointed out that even those organic inhibitors, which show a parallelism between their activity and light absorption, act more efficiently when present in the solution of hydrogen peroxide than when in a separate screening solution. This phenomenon indicates, according to Anderson and Taylor, that the photochemical decomposition of hydrogen peroxide is accompanied by the emission and reabsorption of fluorescent light. Thus secondary radiation will likewise be absorbed by the inhibitors. Anderson and Taylor are of opinion that it is not the hydrogen peroxide molecules, as assumed by Miss Kornfeld, but the ion OOH' , which is responsible for the photosensitivity of this reaction.

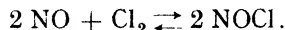
Views regarding the mechanism of the decomposition of hydrogen peroxide have been modified by the experiments of Rice and collaborators (*J. Amer. Soc.* **48**, 2099, 3019 (1926); *J. Phys. Chem.* **31**, 1352, 1587 (1927)), who showed that the submicroscopic dust particles ordinarily present in all hydrogen peroxide solutions have a marked catalytic influence on the velocity of the photochemical decomposition of hydrogen peroxide. Rice is of the opinion that the law of photochemical equivalence is nearly valid for the decomposition of optically clear solutions of hydrogen peroxide, prepared by ultra filtration and other methods. He advances the view, however, that the presence of dust particles plays an important rôle in other photochemical reactions which deviate from the equivalence law.

W. Kistiakowsky (*Z. physik. Chem.* **35**, 431 (1901)) observed that potassium ferri and ferrocyanides accelerate the decomposition of H_2O_2 in light, that this acceleration persists even in the dark, and that it is an example of photochemical after-effect. Kistiakowsky showed with an ultra-microscope that this acceleration is due to the action of a colloidal product of the decomposition of complex iron cyanides. It seems probable that in presence of H_2O_2 colloidal ferric hydroxide is formed from solutions of the iron cyanides in presence of light (compare Haber, *Z. Elektrochem.* **11**, 846 (1905); Foster, *J. Chem. Soc.* **89**, 812 (1906); and Baudisch and Bass, *Ber.* **55**, 2698 (1922)).

The thermal, photochemical, and catalytic decomposition of hydrogen peroxide is undoubtedly very complicated, and is highly susceptible to traces of impurities.

DECOMPOSITION OF NITROSYL CHLORIDE.

Trautz and collaborators (*Z. anorg. Chem.* **88**, 285 (1914); **97**, 241 (1916); **110**, 248 (1920)) studied the kinetics of the reaction in the dark:



They reported that the formation of nitrosyl chloride is an apparently trimolecular reaction, but the actual mechanism may be that of a bimolecular process. The velocity of this reaction is readily measurable at room temperature, and since the equilibrium constant

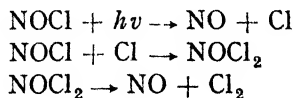
$$K = \frac{[\text{NO}]^2 \times [\text{Cl}_2]}{[\text{NOCl}]^2}$$

is small at ordinary temperatures, consequently the formation of nitrosyl chloride is practically complete. Kiss (*Rec. trav. Chim. Pays-Bas.* **42**, 665 (1923)) found that nitrosyl chloride is partially decomposed by visible light, and that on longer exposure a stationary state is reached. Kiss did not measure the light absorption, but suggested that the velocity of decomposition on illumination could be represented by the equation:

$$-\frac{d[\text{NOCl}]}{dt} = K_1[\text{NOCl}] - K_2[\text{Cl}_2][\text{NO}]^2,$$

where K_2 is the velocity constant of the formation of nitrosyl chloride in the dark. The unimolecular nature of the light reaction suggests that the total radiation of an incandescent lamp used in the experiments of Kiss was only slightly absorbed by nitrosyl chloride. Kiss found that the temperature coefficient for the photochemical reaction is of the order of unity.

Bowen and Sharp (*J. Chem. Soc.* **127**, 1026 (1925)) studied the reaction in radiations of wavelengths 4380—5000 Å, which were markedly absorbed by nitrosyl chloride. Instead of using mixtures of nitrosyl chloride with chlorine, as was done by Kiss, Bowen and Sharp investigated the decomposition of pure nitrosyl chloride, and showed that it is a zero order reaction up to 10% decomposition. The quantum yield is about two molecules of nitrosyl chloride decomposed per absorbed quantum. Bowen and Sharp suggest the following mechanism for the reaction:



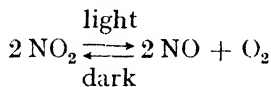
of which the first reaction requires 45000 calories, a value which is less than the amount supplied by the quantum of incident radiation.

According to Cario and Kistiakowsky, the absorption spectrum of NOCl consists of several well defined bands in the region 7000—3500 Å. This probably indicates that excited molecules are formed on light absorption, and that no dissociation takes place immediately.

Recently Kistiakowsky (*J. Amer. Chem. Soc.* **52**, 102 (1930)) has observed the quantum yield 2 in the photochemical decomposition of nitrosyl chloride in radiations of wavelengths from 6300 to 3650 Å. The absorption spectrum of nitrosyl chloride indicates that it possesses a banded structure throughout the visible part of the spectrum. The author has concluded that the mechanism of the photo-decomposition of nitrosyl chloride consists in the formation of an excited molecule, and the collision of the excited molecule with another nitrosyl chloride molecule to yield the decomposition products. According to Schumacher and Sprenger (*Z. Elektrochem.* **35**, 653 (1929)) NO₂Cl is formed by the interaction of NOCl and O₃.

PHOTOCHEMICAL EQUILIBRIUM IN NITROGEN PEROXIDE.

Norrish (*J. Chem. Soc.* 761 (1927), 1158, 1604, 1611 (1929)) has made a detailed study of this photochemical equilibrium. He has shown that when nitrogen peroxide is exposed to radiations from a mercury vapour lamp, it undergoes a reversible decomposition and reaches a state of photochemical equilibrium represented by the equation:



Bodenstein and Lindner (*Z. physik. Chem.* **100**, 87 (1922)) have shown that the dark reaction between NO and O₂ is a trimolecular one. The thermal change $2 \text{ NO}_2 \rightleftharpoons 2 \text{ NO} + \text{ O}_2$ was studied by Bodenstein, Boes, Lindner, and Ramstatter (*Ibid.* **100**, 68 (1922)), who found that the decomposition occurs as a homogenous bimolecular reaction, taking place with measurable velocity over the temperature range 300°—400° with a temperature coefficient of 1.5 for a 10° rise.

Dickinson and Baxter (*J. Amer. Chem. Soc.* **50**, 774 (1928)) have also studied the photochemical decomposition of nitrogen peroxide at low pressure, where the reverse dark reaction is insignificant. By freezing out the residual nitrogen peroxide and the nitric oxide produced, these authors were able to measure the extent of the light reaction from

the oxygen formed, and to determine its quantum efficiency for the series of wavelengths 4360 Å, 4050 Å and 3650 Å. Their results seemed to show the existence of a sharp photochemical threshold in the blue part of the spectrum, as will be seen in the following table:

Wavelength in Å	4360	4050	3650
Quantum yield	0.0092	0.72	1.54

By using a photoelectric cell to measure the light intensity, Norrish has also determined the quantum yield of the reaction, and his results are as follows:

Wavelength in Å	5750	5460	4360	4050	3650	3160—2560
Quantum yield	0	0	0	0.74	2.10	2.07

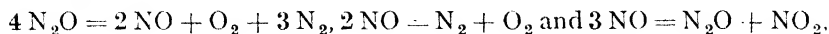
On comparing the data relating to the homogenous thermal and photochemical decompositions of nitrogen peroxide, Norrish has concluded that far more energy is required to decompose the molecule photochemically than thermally. It appears that a part of the light energy absorbed by the molecules of nitrogen peroxide is given out as fluorescence.

Norrish has been able to detect and photograph the fluorescent light given out by nitrogen peroxide. Blue light (4360 Å) produces an orange luminescence and violet light (4050 Å) a greenish yellow luminescence. The spectra show identical structures, involving in the main two wide maxima at 6400 Å and 5900 Å respectively, but with violet light the relative intensity of the former maximum is much less than with blue light. Under similar conditions there is an extremely faint fluorescence with ultra-violet light of 3650 Å. The fluorescence appears at a pressure of 1 mm., and continues till the pressure is as high as 100 mm.

DECOMPOSITIONS OF NITROUS AND NITRIC OXIDES.

Macdonald (*J. Chem. Soc.* 1 (1928)) has investigated the photo-decomposition of nitrous and nitric oxides, using light of wavelengths 1860—1990 Å. There is no induction period in the photo-decomposition of nitrous oxide. The quantum yield was found to be 3.9 for nitrous oxide and 0.73 for nitric oxide. The quantum yield in the case of nitrous oxide appears to be constant over the temperature range 0°—40°, and up to a pressure of one atmosphere. The absorption coefficient of nitrous oxide increases 1.47 times for a 10° rise. In the experiments, pressures of about 20—650 mm. and exposures varying from 2 to 66.5 minutes were employed. It is shown that nitrous oxide absorbs

light much more strongly than does nitric oxide. Beer's law holds strictly for both gases. The gases decompose according to the following equations:



the former reaction for nitric oxide predominating.

Dhar (*Z. anorg. Chem.* **159**, 103 (1926)) has suggested that in many photochemical reactions a cluster containing an ion and the reacting substances is formed. Moreover, the high quantum yield in certain photochemical reactions has its analogy in chemical changes induced by α particles. Recently B. Lewis (*Nature* **121**, 792 (1928)) has suggested that clustering takes place in the photochemical decomposition of nitrous oxide.

DECOMPOSITION OF NITROUS ACID.

Mukerji and Dhar (*Z. Elektrochemie* **31**, 255 (1925)) have shown that the decomposition of nitrous acid according to the equation $3 \text{HNO}_2 \rightleftharpoons \text{HNO}_3 + 2 \text{NO} + \text{H}_2\text{O}$ is accelerated by sunlight. The velocity of the reaction follows the unimolecular formula. The following results have been obtained in the dark, and in sunlight at 30° :

Concentration of nitrous acid	N/32	N/64	N/128
K_1 (in dark in open vessels)	0.00562	0.00516	0.00299
K_1 (in dark in closed vessels)	0.00135	0.00134	0.00129
K_1 (in sunlight in open vessels)	0.00589	0.00570	0.00312
K_1 (in sunlight in closed vessels)	0.00329	0.00293	0.00187

The experimental results show that the influence of light is more pronounced in the decomposition taking place in closed vessels than in that in open ones. Moreover, the velocity of the reaction both in the light and in the dark is much greater in open vessels than in closed ones. This is attributed to a displacement of equilibrium owing to the removal of nitric oxide, which is a product of the decomposition, in the reaction taking place in open vessels, and thus the velocity is increased.

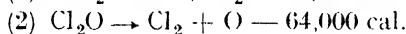
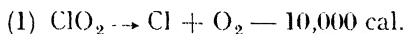
Recently, Murti and Dhar have studied this decomposition in detail, in the total light from a 1000 Watt gas filled tungsten filament lamp, and in radiations of wavelengths 4725 Å and 5650 Å. The decomposition is appreciably accelerated even by radiations of wavelengths 7304 Å and 8500 Å. The temperature coefficient of the light reaction is less than unity between 40° and 30° and 50° and 40° . The quantum yield is greater than unity, and varies from 1.2 to 15, depending on the

wavelength and temperature. It is observed that the velocity of the reaction is proportional to the cube root of the intensity of the incident light or absorbed radiation.

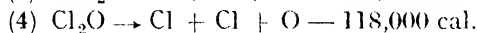
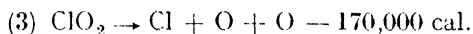
DECOMPOSITION OF OXIDES OF CHLORINE.

Bowen (*J. Chem. Soc.* **123**, 1199 (1923)) investigated the decomposition of chlorine monoxide, and of chlorine dioxide dissolved in CCl_4 , in presence of blue light of wavelength 4100—4700 Å. Both the reactions are proportional to the amount of absorbed light energy; the concentration of the dioxide was varied from 0.32 to 0.035 mols per litre and that of the monoxide from 0.14 to 0.085 mols per litre. The light intensity was varied in the ratio 1 : 6. For the average wavelength 4450 Å, Bowen obtained for chlorine dioxide the quantum yield 0.83, and for chlorine monoxide 0.90.

Bowen suggested the following mechanism for these reactions:



The energy for the quanta of blue light is equal to about 64,000 calories, being too small for the following reactions:



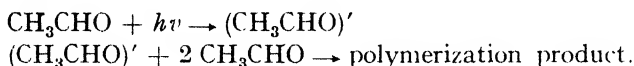
The mechanism suggested seems improbable, because the free atoms of oxygen or chlorine are likely to react with oxides of chlorine present. It appears, therefore, that if Bowen's mechanism is correct, the quantum yield should have been greater than unity. As a matter of fact, the quantum yield in many exothermal photochemical reactions is much greater than unity, and as the decomposition of chlorine monoxide and dioxide are exothermal reactions, the quantum yield is expected to be greater than unity.

DECOMPOSITIONS OF ACETALDEHYDE AND ACETONE.

The decomposition of acetaldehyde was first studied by Berthelot and Gaudechon (*Compt. rend.* **156**, 68, 233 (1913)) in the liquid phase. In radiations of wavelengths longer than 3000 Å, acetaldehyde is mostly decomposed into CO and CH_4 , only traces of C_2H_6 being formed. Shorter wavelengths (3000—2500 Å) cause a polymerization and a partial oxidation of acetaldehyde to acetic acid. Wavelengths

shorter than 2500 Å cause a rapid polymerization to paraldehyde and metaldehyde. Since there was mercury in the reaction vessels of Berthelot and Gaudechon the possibility of photosensitization by activated mercury vapour is not excluded.

Bowen and Watts (*J. Chem. Soc.* **127**, 1607 (1925)) reported that acetaldehyde vapour, under the action of ultra-violet light of a mercury lamp, partly decomposes into CO and CH₄ and partly polymerises. The authors assume that the following reactions take place:



The observed quantum yield for the wavelength 3130 Å is 2·17.

Bowen and Watts studied the decomposition of gaseous acetone in ultra-violet light and obtained varying quantum yields depending on the pressure of the gas. At higher pressures the quantum yield was 1·7 and at lower pressures and at room temperature 0·41.

The products of the photochemical decomposition of acetone have been studied by Berthelot and Gaudechon (compare *Travaux scientifiques de D. Berthelot*, Paris 1917, pp. 116—146).

DECOMPOSITION OF OXALIC ACID.

Hanssen (*Compt. rend.* **145**, 564 (1907)) asserted that the photo-decomposition of oxalic acid follows the law of mass reaction. Berthelot and Gaudechon (*Compt. rend.* **158**, 1791 (1914)) were the first to investigate this reaction in detail, and observed that the products formed depend on the spectral distribution of the incident radiation. Thus, in light of wavelength longer than 2500 Å, formic acid and a gaseous mixture containing about 89 per cent carbon dioxide and 11% CO were formed, but in light of shorter wavelengths the substances formed from the reaction were CO₂ 67%, H₂ 33%, and traces of formaldehyde (observed also by Baly, Heilbron, and Barker, *J. Chem. Soc.* **119**, 1025 (1921)). Berthelot and Gaudechon suggested that oxalic acid is quantitatively decomposed according to the equation: H₂C₂O₄ → HCOOH + CO₂ by rays shorter than 3000 Å, and that the formic acid produced undergoes a photochemical decomposition, according to the equation HCOOH → H₂O + CO in radiations of wavelength 2500—3000 Å, or according to the scheme HCOOH → H₂ + CO₂ in very short ultra-violet rays.

Recently Allmand and Reeve (*J. Chem. Soc.* **129**, 2834 (1926)) found that oxalic acid is quantitatively decomposed into formic acid and

carbon dioxide, in agreement with the observations of Berthelot and Gaudechon. Neither carbon monoxide nor hydrogen was obtained among the gaseous products of the reaction, but small amounts of formaldehyde were detected. The following results were obtained by Allmand and Reeve regarding the quantum yield in radiations of different wavelengths:

Wavelength in Å	2650	3000	3650
Quantum yield	0.0100	0.0041	0.00095

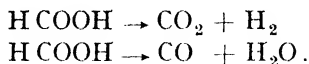
It is interesting to note that these values of quantum yield are very small in comparison with the yield of unity for the decomposition of oxalic acid in presence of uranium salts obtained by Büchi (*Z. physik. Chem.* **111**, 269 (1924)).

Berthelot and Gaudechon (*Compt. rend.* **152**, 262 (1911); **158**, 1791 (1914)) showed that solid oxalic acid decomposes under the action of ultra-violet light. Noyes (junior) and Kouperman (*J. Am. Chem. Soc.* **45**, 1398 (1923)) showed that the velocity of this decomposition increases in light of shorter wavelengths. Water accelerates this reaction, as the anhydrous acid decomposes more slowly than the hydrated crystals. There is a long induction period, and after the induction period the rate of decomposition is practically constant.

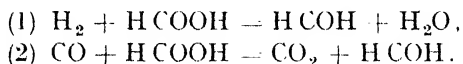
DECOMPOSITION OF FORMIC ACID.

Allmand and Reeve (*J. Chem. Soc.* **129**, 2852 (1926)) contradicted the view of Berthelot and Gaudechon that the CO and H₂ obtained by them during oxalic acid decomposition are really due to the decomposition of formic acid, which is formed from oxalic acid, and which is decomposed in two different ways according to the frequency of the absorbed radiation. The results of analysis of the gaseous product obtained on illumination of formic acid by Allmand and Reeve, showed that the relative amounts depend largely on the concentration of the formic acid solution, but not on the wavelength of absorbed radiation, as assumed by Berthelot and Gaudechon. According to Allmand and Reeve a 2.4 N solution of formic acid gave large amounts of CO₂ and much formaldehyde, which is a condensation and a reduction product of CO₂, and only small amounts of CO and H₂. On the other hand, from a 0.113 N solution the yield of CO and H₂ relative to CO₂ was markedly increased, but no formaldehyde was observed. Commenting on these results, Allmand and Reeve suggested that formic acid

molecules can be decomposed in two different ways independent of the wavelengths of the absorbed radiation. The alternative reactions are:



They determined the relative amounts of the different gases formed on decomposing a dilute solution of formic acid, and stated that the first reaction occurs about six times more often than the second one. Allmand and Reeve advanced the view that amongst the molecules formed in the primary decompositions of formic acid, activated molecules of H_2 and CO possess initially large amounts of energy, and are capable of reacting on collision with formic acid molecules:



In more dilute solutions these activated molecules lose their energy by collision with the water molecules before meeting formic acid molecules: hence no secondary reactions take place in dilute solutions. The following values of quantum yield were obtained by Allmand and Reeve with different wavelengths:

Formic acid 2.4 N.			
Wavelength in Å	2600	3000	3600
Quantum yield	2.7	1.06	very small

These values, when compared with those of oxalic acid decomposition, show that the quantum yield with formic acid decomposition decreases rapidly in the spectral region 3000 Å to 3600 Å, but that the ratios of the quantum yields of both the acids for the wavelengths 2600 Å and 3000 Å are nearly the same.

Ramsperger and Porter (*J. Amer. Chem. Soc.* **48**, 1267 (1926)) investigated the photochemical decomposition of gaseous formic acid in the total radiation of a mercury arc transmitted by quartz. They observed 64% of $\text{CO} + \text{H}_2\text{O}$ and 36% CO_2 and H_2 , on complete decomposition of the gaseous acid. These results show that the relative velocities of the two types of decomposition of formic acid, as suggested by Allmand and Reeve ($\text{H COOH} \rightarrow \text{CO} + \text{H}_2\text{O}$, $\text{H COOH} \rightarrow \text{CO}_2 + \text{H}_2$), are quite different in the gaseous state and in the aqueous solution. It should be noted here that Taylor and Bates (*J. Amer. Chem. Soc.* **48**, 2840 (1926)), studying the decomposition of formic acid vapour sensitized by mercury atoms, obtained a different ratio $(\text{CO} + \text{H}_2\text{O}) : (\text{CO}_2 + \text{H}_2) = 76 : 24$. Further work is necessary to find out the cause of the differences in the ratios obtained in different conditions.

Herr and Noyes (jun.) (*J. Amer. Chem. Soc.* **50**, 2345 (1928)) have shown that for liquid formic acid the quantum efficiency rises with increasing frequency. Formic acid vapour absorbs radiations of short wavelengths only. The primary reaction in both the liquid and vapour states may lead to the formation of carbon dioxide.

DECOMPOSITION OF PERMANGANATE IONS.

Rideal and Norrish (*Proc. Roy. Soc. A* **103**, 342, 366 (1923)) tried to show that the Einstein law of photochemical equivalence is applicable to the photochemical decomposition of permanganate ions in ultra-violet light. Rideal and Norrish reported that the visible spectrum in which permanganate ions show several absorption bands is photochemically inactive, but that ultra-violet light of wavelength 3130 Å, where permanganate possesses an absorption maximum, causes its decomposition, and the formation of colloidal MnO_2 . Although the active radiation is completely absorbed by a solution of N/100 KMnO_4 the velocity of the reaction is unimolecular with respect to the permanganate ion. Apparently the reaction is not proportional to the absorbed light energy. Rideal and Norrish advanced the view that in reality the velocity of the decomposition is proportional to the absorbed light energy, but that during the course of the reaction the scattering of light by the colloidal MnO_2 particles formed increases very rapidly, and thus the light energy actually absorbed by permanganate diminishes considerably. It appears that the arguments advanced in favour of the proportionality of the velocity of reaction and the light energy absorbed are unsatisfactory. Rideal and Norrish determined the quantum yield, and obtained the value 0.2 in radiations of wavelengths 3650 to 2536 Å. In presence of sulphuric acid the quantum yield approaches 0.5. In presence of oxalic acid Rideal and Norrish observed a much more rapid reaction, but the kinetics of this process were not quantitatively studied by them. (Compare Dhar and collaborators, *Z. Elektrochem.* **32**, 586 (1926); *Z. anorg. Chem.* **176**, 373 (1928)).

DECOMPOSITIONS OF POTASSIUM COBALTIOXALATE, SODIUM COBALTINITRITE, AND OTHER COBAL TIC COMPLEXES.

Vraněk (*Z. Elektrochem.* **23**, 336 (1917)) studied the decomposition of potassium cobaltioxalate, which is changed into cobaltous oxalate, potassium oxalate, and oxygen when exposed to light. The velocity of the reaction in dilute solutions is approximately proportional to the

absorbed light energy. As the reaction proceeds, it is retarded by potassium oxalate, which is a product of the chemical change. The photo-decomposition appears to be unaffected by dilute acids. The absorption spectrum of potassium cobaltioxalate consists of two well defined bands with absorption maxima at about 6050 and 4260 Å. Vraněk's results on quantum yields, which are recorded below, show that all absorbed wavelengths are not photochemically active, but that only wavelengths shorter than 4900 Å can induce the decomposition, and that the quantum yield increases markedly with the frequency of the radiation:

Decomposition of potassium cobaltioxalate				
Wavelength in Å	4920	4360	4050	3650
Quantum yield	0.0	0.6	0.9	1.5

The quantum yield is independent of the concentration of potassium cobaltioxalate between the limits 0.0002 to 0.005 M. Vraněk pointed out that the three higher values of quantum yield, plotted against wavelength, lie on a straight line. Its continuation indicates a quantum yield of zero at a wavelength close to 4900 Å, and this was verified by experiments. The photochemical decomposition of potassium cobaltioxalate appears to be one of those reactions in which the relation between velocity and wavelength of incident radiation is not in agreement with the equivalence law.

Recently, this reaction has been re-investigated by Bhagwat and Dhar. They find that the reaction is unimolecular in the dark, and in the light from a 1000 Watt gas-filled tungsten filament lamp. But in sunlight the reaction is zero molecular. Measurements of absorbed light energy have shown that the absorption in sunlight is much greater than in the artificial light; and this seems to account for the zero molecular constants obtained in sunlight. In the artificial light the velocity of the reaction is directly proportional to the intensity of the incident light; whereas in sunlight the square root relation obtains between the velocity of the reaction and the intensity of the incident light. The temperature coefficients in sunlight, in artificial light, and in the dark are 1.13, 1.18 and 3.7 respectively. The quantum yield is unity in sunlight, but it is less than unity in artificial light.

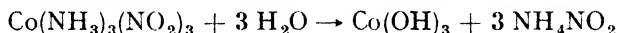
The temperature coefficient of the photochemical decomposition of potassium cobaltioxalate has the value 1.06, whilst the temperature coefficient of the thermal reaction has the high value 4.2.

Vraněk observed that, as the solutions became more dilute, the unimolecular coefficients tended to fall off, and to give way to

bimolecular coefficients. According to Vraněk, the velocity of the photochemical decomposition of potassium cobaltioxalate is directly proportional to the light intensity.

Jaeger and Berger (*Rec. trav. chim.* **40**, 153 (1921)) observed that the effect of neutral salts on the velocity of decomposition of potassium cobaltioxalate is quite appreciable.

Schwarz and Weiss (*Ber.* **58B**, 746 (1925)) studied the decomposition of aqueous solutions of some complex cobaltic amminonitrites under the influence of violet and ultra-violet light. They suggest that the reactions are cases of hydrolysis, as for example:



The course of decomposition is nearly unimolecular, but experiments with certain concentrations indicate a reaction of zero order. The photosensitivity of this class of complex cobaltic salts increases with the number of nitrite groups present in the molecules. In these cases also, according to Schwarz and Weiss, the mercury line 4920 Å is still practically photochemically inactive, and the light efficiency increases towards the shorter wavelengths.

Schwarz and Tede (*Ber.* **60B**, 63 (1927)) have shown that, from the photochemical decomposition of cobalt-tetrammine salts in aqueous solution according to the equation $[\text{Co}(\text{NH}_3)_4x_2]y + 3 \text{H}_2\text{O} = \text{Co}(\text{OH})_3 + 2 \text{NH}_4x + \text{NH}_4y + \text{NH}_3$, it can be deduced that the stability of the cobalt complexes is in the following order, $\text{CO}_3'' > \text{C}_2\text{O}_4'' > \text{NO}_2' > \text{Br}' > \text{Cl}' > \text{SO}_4''$, where these radicals are substituted for x in the cobaltic salt. In the pentammine series, the sequence is $\text{CO}_3'' > \text{Cl}' > \text{C}_2\text{O}_4'' > \text{SO}_3'' > \text{NO}_2' > \text{NO}_3' = \text{SO}_4''$. Examination of the photochemical decomposition of the stereoisomeric salts $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2]\text{NH}_4$ shows that the dark brown is less stable than the reddish brown variety.

Recently, Berger (*Rec. trav. Chim.* **44**, 49 (1925)) showed that the photochemical decomposition of various complex cobaltic salts is a reduction of the trivalent cobalt atom and not a hydrolysis, as suggested by Schwarz and Weiss. The resulting $\text{Co}(\text{OH})_2$ is, however, rapidly oxidised by oxygen of the air to $\text{Co}(\text{OH})_3$. Berger carried out his experiments with dilute acid solutions of a number of cobaltic salts containing NO_2 , C_2O_4 , NH_3 and C_2H_4 groups in the complex. Of these, the first two groups caused a pronounced photosensitiveness. The influence of different neutral salts on the reaction-velocities is nearly of the same order of magnitude as in the decomposition of potassium cobaltioxalate.

Recently Bhattacharya and Dhar (*Z. anorg. Chem.* **176**, 372 (1928)) quantitatively investigated the photochemical decomposition of aqueous solutions of sodium cobaltinitrite at different temperatures, and under the influence of radiations of different wavelengths. The reaction takes place according to the following equation: $2 \text{Na}_3\text{Co}(\text{NO}_2)_6 + \text{H}_2\text{O} = 6 \text{NaNO}_2 + 2 \text{Co}(\text{NO}_2)_2 + 2 \text{HNO}_2 + \text{O}$, and the experimental results are recorded below:

$\text{M}/10 \text{Na}_3\text{Co}(\text{NO}_2)_6$

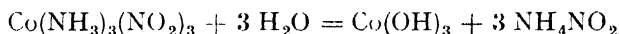
Wavelength of light	Temperature in °C	K_1 unimolecular	Temperature Coefficient	Quantum Yield
Dark	20	0.000589	3.5	—
	30	0.00208	3.04	—
	40	0.00632		
Sunlight	20	0.121	1.64	240
	30	0.199	1.58	231
	40	0.317		614
4725 Å	20	0.00132	2.34	3.75
	30	0.00379	2.21	9.4
	40	0.0101		17.4
5650 Å	20	0.00104	2.5	2.24
	30	0.00321	2.4	4.6
	40	0.00903		9.6
7304 Å	20	0.000804	2.7	1.1
	30	0.00266	2.6	2.5
	40	0.00783		6
8500 Å	20	0.000730	3.05	0.92
	30	0.00251	2.84	1.3
	40	0.00754		3.9

The decomposition of sodium cobaltinitrite in the dark as well as in light is unimolecular, and the temperature coefficient for a 10° rise in the dark has the value 3.5, whilst in light the temperature coefficient falls off, and the greater the acceleration in light the smaller is the temperature coefficient. From the foregoing results on quantum yield it will be at once evident that the quantum yield is much greater in sunlight than in radiations of wavelengths 4725 Å, 5650 Å and 7304 Å. Exactly similar results have been obtained by us with more than 40 photochemical reactions. The quantum yields for the hydrogen-chlorine reaction and the decomposition of ammonia in

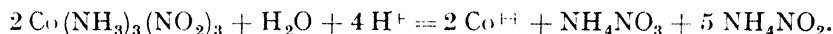
white light are much greater than those obtained by the summed reactions of the different parts of the spectrum (compare Kuhn, *Compt. rend.* **177**, 956 (1923)).

The velocity of the decomposition of sodium cobaltinitrite in sunlight and in light from a 1000 Watt gas-filled tungsten filament lamp is proportional to the square root of the incident radiation when it is varied in the ratio 1 : 25.

Very recently Luther and Frieser (*Z. Elektrochem.* **36**, 141 (1930)) have shown that in neutral and alkaline solutions trinitro-triammine cobalt decomposes in the dark and in light according to the equation :



and in acid solutions the reactions is



In the dark, there is an intermediate product, which also undergoes change in the dark as well as in light. The temperature coefficient of the dark original reaction in acid solution between 65° and 55° = 4.4, and that of the reaction involving the intermediate product = 3.5. Both the dark reactions are unimolecular. The quantum yield of the original reaction in radiation of wavelength 3660 Å is 0.2, and the temperature coefficient has the value 1.03. The quantum yield of the reaction involving the intermediate product is 0.37, in radiation of wavelength 3660 Å. The order of the light reactions is zero, and the radiation 3660 Å is highly absorbed. The authors have carefully measured the extinction coefficients of the original solution, intermediate, and end products.

DECOMPOSITION OF POTASSIUM MANGANIOXALATE.

Christiansen (*Z. anorg. Chem.* **27**, 325 (1911)) was the first to observe that crystals of potassium manganioxalate decompose in the dark and rapidly in light.

Ghosh and Kappanna (*J. Indian Chem. Soc.* **3**, 127 (1926)) have investigated the photolysis of an aqueous solution of potassium manganioxalate, and have obtained the quantum yield 1.28 in radiation of wavelength 4880 Å. The velocity of the reaction is almost directly proportional to the light intensity in blue light. The quantum yield does not change on the addition of an excess of potassium oxalate.

The temperature coefficient (between 16° and 26°) for the dark reaction is 2.06 in neutral oxalate solution, and 3.30 in oxalate solution

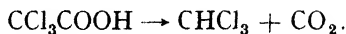
containing 2.0 grs. of oxalic acid per litre. The temperature coefficient for the light reaction is about 1.3.

Potassium manganioxalate in solution is coloured pinkish red, and has been found to have absorption in all regions of the spectrum. In the region 5790 Å Beer's law is obeyed by solutions of this salt.

Ghosh and Kappanna have observed that the velocity of the photolysis of potassium manganioxalate is practically the same in ordinary and plane polarized light, but in circularly polarized light the velocity is slightly greater. The effect of adding oxalic acid is to depress the velocity of decomposition both in darkness and in light.

DECOMPOSITION OF TRICHLORACETIC ACID.

Banerji and Dhar (*Z. anorg. u. allg. Chem.* **2**, 172 (1924)) have observed that this reaction is photosensitive. The reaction takes place according to the following equation:



The following are the results obtained:

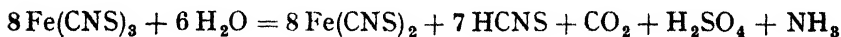
N/10 trichloroacetic acid.

Condition	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark " K_1 "
Sunlight	75	0.001488	3.6
	85	0.005466	
Dark	80	0.002223	4.29
	90	0.009540	

Further work on this reaction with monochromatic light is in progress in the author's laboratory.

DECOMPOSITION OF FERRIC THIOCYANATE.

Philip and Branley (*J. Chem. Soc.* **103**, 795 (1913)) represented the decomposition of this compound in the diffused light of the laboratory by the equation:



Bhattacharya and Dhar (*J. Indian Chem. Soc.* **6**, 144 (1929)) observed that this decomposition is highly photosensitive, and that the velocity of the reaction in the dark is negligibly small. The concentrations could be accurately measured by a spectrophotometer. The following results were obtained:

N/250 Ferric Chloride and N/50 Ammonium Thiocyanate 10 c.c. each.

Region in Å	Temperature in °C	K_1 Monomolecular	Temperature Coefficient after deducting the dark reaction	Quantum Efficiency
$\lambda = 4725$	20	0.000509		6.3
	30	0.00107	2.12	9.2
	40	0.00215	2.0	12.4
$\lambda = 5650$	20	0.000392		5.6
	30	0.000902	2.3	7.3
	40	0.00197	2.2	11.1
$\lambda = 7304$	20	0.000284		3.4
	30	0.000709	2.5	4.6
	40	0.00163	2.3	7.3
$\lambda = 8500$	20	0.000173		2.5
	30	0.000471	2.72	3.9
	40	0.00123	2.61	5.6

Light absorption:

Region in Å	7000	6707	5970	5670	5490	5320	5200
Extinction coefficient	0.05	0.09	0.10	0.42	0.73	1.46	2.07
Region in Å	5000	4910	4800	4720	4670	4550	4400
Extinction coefficient	3.8	Beyond α		Complete absorption			

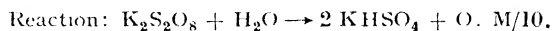
The decomposition of ferric thiocyanate is proportional to the square root of the change in intensity of the incident light from a 1000 Watt lamp.

DECOMPOSITION OF SOLUTIONS OF POTASSIUM PERSULPHATE.

This reaction was investigated by Green and Masson (*J. Chem. Soc.*, **97**, 2083 (1910) in the dark. Dhar (*Proc. Akad. Wetensch. Amsterdam*, **23**, 308 (1920)) was the first to show that the reaction is markedly photosensitive. Recently Morgan and Crist (*J. Amer. Chem. Soc.* **49**, 16, 33, 960 (1927)) and Kailan (*Montash.* **44**, 35 (1923)) have studied the reaction under the influence of light from a quartz mercury lamp.

Morgan and Crist have found that the velocity of the reaction is proportional to the intensity of the light, and that the temperature coefficient of the reaction is 1.18 in light.

Bhattacharya and Dhar (*Z. anorg. u. allg. Chem.* **176**, 372 (1928)) have determined the kinetics, temperature coefficient, and quantum efficiency of this reaction in sunlight.



Condition	Temperature in °C	K_0 Zeromolecular	Temperature Coefficient after deducting the dark reaction	Quantum Efficiency
Dark	17	0.000071	---	---
Sunlight	17	0.0190	1.2 1.18	130
	27	0.0228		230.5
	37	0.0269		269

The decomposition of potassium persulphate is proportional to the square root of the change in intensity of the incident light, the source of light being the sun.

Morgan and Crist (*J. Amer. Chem. Soc.* **49**, 960 (1927)) studied this reaction in light from a quartz mercury lamp. They observed that this decomposition is directly proportional to the change in intensity of light. Hence it appears that the relation between the velocity of this reaction and the intensity of light is variable.

DECOMPOSITION OF SODIUM HYPOCHLORITE AND OTHER OXYACIDS OF CHLORINE AND THEIR SALTS.

The decomposition of sodium hypochlorite solution was first studied by Lewis (*J. Chem. Soc.* **101**, 2371 (1912)), and extended by his pupil Spencer (*ibid.* **105**, 2565 (1914)). It was observed that the decomposition is caused by the spectral region 4360—3130 Å of a uviol mercury lamp. Dhar (*Z. anorg. Chem.* **121**, 156 (1922)) showed that the reaction is semimolecular in the total light of the uviol lamp. Spencer reports that the velocity of the reaction is proportional to the absorbed light energy, and that the photochemical efficiency of incident radiation increases with decreasing wavelength. Experiments in monochromatic light showed that with light of wavelength 4050 Å, which is feebly absorbed, a unimolecular velocity coefficient is obtained, whilst in radiation of wavelength 3130 Å, which is largely

absorbed, the reaction becomes zeromolecular. The temperature coefficient of the hypochlorite decomposition has the value 1.06 (Spencer), whilst that of chlorine water decomposition is 1.4 (Benrath and Tüchel). Sodium chloride exerts a very feeble retarding influence, the velocity being decreased about 10% on the addition of 0.34 N NaCl. Allmand and Webb (*Z. physik. Chem.* **131**, 189 (1928)) state that chlorate ion is also formed in small quantities in this photochemical decomposition, and suggest that the oxygen atoms formed in this reaction ($\text{NaClO} \rightarrow \text{NaCl} + \text{O}$) act on the hypochlorite forming ClO_3' ; the hypochlorite ion, being a less active acceptor of oxygen, forms ClO_3' in smaller amounts than the amounts of HClO_3 obtained in the decompositions of HClO and chlorine water. On the other hand, they report that preliminary experiments indicate identical quantum yields in the decompositions of chlorine water, hypochlorous acid, and hypochlorite ion.

Measurements of the quantum yield of the reaction show that at constant frequency, decrease of hypochlorite concentration causes the quantum yield to decrease markedly, whilst increase of frequency causes a great increase of the quantum yield. The Lambert-Beer law appears to be valid for sodium hypochlorite solution products. The extinction coefficients for the mercury lines 4360 Å and 4050 Å are 0.08 and 0.40 respectively.

Dhar and Sanyal (*J. Phys. Chem.* **29**, 926 (1925)) observed that solutions of potassium chlorate decompose in tropical sunlight into potassium chloride and oxygen. Oertel (*Biochem. Z.* **60**, 480 (1914)) and Mathews and Curtis (*J. Phys. Chem.* **18**, 641 (1914)) and others studied qualitatively the photochemical decompositions of other oxyhalogen compounds.

Fowler (*Mem. Manchester Phil. Soc.* **52** XIV, 1 (1908)) has shown that bleaching powder suspension loses its available chlorine with great rapidity on exposure to tropical sunlight.

CHAPTER XII.

Photochemical Hydrolysis.

HYDROLYSIS OF CHLOROPLATINIC ACID AND VARIOUS SALTS.

Kohlrausch (*Z. physik. Chem.* **33**, 257 (1900)) was the first to observe that chloroplatinic acids are hydrolyzed into platinic hydroxide and hydrochloric acid to a greater extent in light than in the dark. This reaction has been investigated in detail by Boll and co-workers (*Compt. rend.* **154**, 881 (1912); **155**, 826 (1912); **156**, 138, 691 (1913); **157**, 115 (1913); **158**, 32 (1914)). Their results indicate that with dilute solutions (2×10^{-5} to 2×10^{-4} N with respect to acid), in which the light absorption is incomplete, the velocity of hydrolysis is bimolecular and proportional to the incident light intensity.

In several publications Dhar and co-workers (*Z. anorg. Chem.* **168**, 209 (1927); *Kolloid. Z.* **42**, 120 (1927)) have shown that aqueous solutions of salts of strong acids and a sparingly soluble weak base are slowly hydrolyzed with the formation of a colloid of the sparingly soluble base. Now light accelerates this slow hydrolysis, which also takes place in the dark. Boll and co-workers have investigated the kinetics and energetics of the hydrolysis of chloroplatinic acids, which process also takes place slowly in the dark, and hence light only accelerates but does not cause this reaction, as was assumed by Boll and co-workers.

Ritchie (*J. Phys. Chem.* **32**, 1269 (1928)) has shown that on exposure to light, ferric chloride solutions become more deeply coloured.

Recently Miss Roy and Dhar have shown that the hydrolysis of ferric, chromic, aluminium, cobalt and nickel salts is accelerated by light. Measurements of the electric conductivity, hydrogen ion concentration, absorption coefficient, and quantum efficiency of this hydrolysis, which is accelerated by light, are in progress in the author's laboratory.

Boll and collaborators state that the quantum yield in the hydrolysis of chloroplatinic acids is proportional to the concentration of the acids, and is independent of the light intensity. The following results were obtained regarding the quantum yield with tetrachloroplatinic acid under the influence of radiations of different wavelengths:

Wavelength Å	2378	2400	2482	2537	2655
Quantum yield	4.7	3.7	2.8	1.9	1.5
Wavelength Å	2970	3100	3660	4350	5460
Quantum yield	0.25	0.070	0.026	0.0033	0.00090

Similar results were obtained by Boll for the hexachloro- and dichloro-platinic acids. The proportionality of the quantum yield to the concentration of the acids could be explained from the view point that the chemical process is a bimolecular reaction, which is caused by the collision of molecules activated by absorption of light with other inactive acid molecules. Further work is necessary for elucidating the mechanism of these reactions involving hydrolysis.

HYDROLYSIS OF MONOCHLORACETIC ACID AND MONOBROMACETIC ACIDS.

Euler and Cassel (*Z. physik. Chem.* **84**, 371 (1913)) first studied the hydrolysis of monochloroacetic acid in the total radiation of a mercury lamp. The unimolecular constants were found to increase with dilution, and HCl acts as a retarder. Rudberg (*Z. Physik.* **24**, 247 (1924)) utilized monochromatic light of wavelength 2536 Å and determined the energy absorbed. When proper corrections for absorption and reflection in glass and water are made, the quantum yield of 1.05 molecules was obtained in the case of 0.5 N and a quantum yield of 0.95 for 0.3 N aqueous solutions of monochloroacetic acid.

The hydrolysis of monobromoacetic acid has a measurable velocity in the dark, and the velocity of the photochemical reaction was obtained by subtracting the dark velocity from the total change observed in light. Because the light absorption is greater with monobromoacetic acid than with monochloroacetic acid, more dilute solutions of monobromoacetic acid were used, and the quantum yields of 0.35 molecules per quantum for 0.02 N and 0.32 for 0.01 N were observed; when an equivalent amount of NaOH was added the yield was 0.47, and when the amount of NaOH was doubled the quantum yield was 0.54. Experiments with Na_2SO_4 showed that the increase in the photochemical yield is due to the presence of OH ions. Though monochloroacetic and monobromoacetic acid are very similar in their properties, the photochemical behaviour of monochloroacetic acid is different from that of monobromoacetic acid. It seems that further work is necessary to settle whether the applicability of the law of equivalence to the hydrolysis of monochloroacetic acid is accidental or not.

HYDROLYSIS OF CANE SUGAR.

A few years ago Lindemann (*Phil. Mag.* **40**, 671, VI (1920)) pointed out that, on the basis of the simple radiation hypothesis, the inversion of cane sugar must be enormously accelerated by sunlight, but he stated that the reaction actually proceeds at the same rate whether it is exposed to sunlight or not. Dhar (*Z. anorg. u. allg. Chem.* **119**, 177 (1921); *Faraday. Soc. Discussion.* 1921) has shown that the statement of Lindemann is not correct, and that a solution of sucrose in tropical sunlight is completely inverted even in absence of acids on long exposure, whilst in presence of hydrochloric acid the inversion is distinctly accelerated by sunlight. In a subsequent communication Banerji and Dhar (*Z. anorg. u. allg. Chem.* **134**, 172 (1924)) investigated the kinetics of sucrose inversion in presence of hydrochloric acid in sunlight, and showed that the temperature coefficient for a ten degree rise of temperature can vary from 3.4 to 2.78 in sunlight, according to the variation in light intensity, whilst the temperature coefficient of the dark reaction has a value 3.82 under the same conditions.

Bhattacharya and Dhar (*J. Indian Chem. Soc.* **6**, 879 (1929)) have now determined the kinetics, temperature coefficients, and quantum efficiency of the hydrolysis of sucrose in light of different wavelengths.

The velocity of the hydrolysis of sucrose was determined by a polarimeter.

In order to determine the light absorption of cane sugar in different parts of the visible spectrum, the extinction coefficients have been measured by a Nutting spectrophotometer.

The following are the experimental results:

20% cane sugar, 15 c.c., and N/20 HCl, 5 c.c.

Condition	Temperature in °C	K_1 Mono- molecular	Temperature Coefficient after deducting the dark reaction K_{45}/K_{35}	Quantum Efficiency
Dark	30	0.0000975	3.85	
	35	0.000189		
	45	0.000727		
$\lambda = 4725 \text{ \AA}$	30	0.000147	3.18	455
	35	0.000278		630
	45	0.00101		—

20% cane sugar, 15 c.c., and N/20 HCl, 5 c.c. (Continued).

Condition	Temperature in °C	K_1 Mono- molecular	Temperature Coefficient after deducting the dark reaction K_{45}/K_{35}	Quantum Efficiency
$\lambda = 5650 \text{ \AA}$	30	0.000125	3.32	250
	35	0.000242		385
	45	0.000903		—
$\lambda = 7304 \text{ \AA}$	30	0.0001096	3.7	145
	35	0.000212		162
	45	0.000812		—
1000 Watt lamp	35	0.000548	—	16.5×10^2
$\lambda = 8500 \text{ \AA}$	30	0.000101	3.75	112
	35	0.000203		142
	45	0.000780		—

Light absorption:

Region in Å	7000	6500	5970	5600	5000	4800	4720	4550	4400
Extinction coefficient	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14

From the results it is observed that Einstein's law of photochemical equivalence is not at all applicable. The quantum efficiency increases with temperature and the frequency of the incident radiation. The temperature coefficients of the photochemical changes are less than those of the corresponding thermal reactions. The greater the acceleration in light of different wavelengths, the less the temperature coefficient.

The ratio of the velocity of this photochemical reaction and the intensity of the incident light varies between the limits $1-\frac{1}{3}$; the particular value obtained is determined by the degree of acceleration of the photochemical reaction over the thermal reaction. From a survey of the results of different workers, the author suggests that the above phenomenon is a general one. This will be more fully discussed in Chapter XXI. Suffice it to say here that the ratio of the velocity of the reaction and the intensity of the incident light can be varied for one and the same photochemical reaction by varying the experimental conditions.

CHAPTER XIII.

Photochemical Polymerizations.

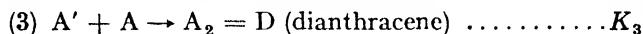
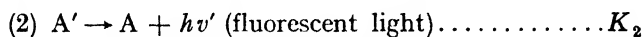
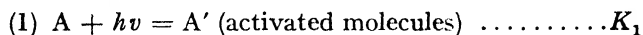
POLYMERIZATION OF ANTHRACENE.

This reaction has been extensively studied by Luther and Weigert (*Z. physik. Chem.* **51**, 297 (1905); **53**, 385 (1905)) and Weigert (*Ber.* **42**, 850 (1909)). It was observed that anthracene, whether solid, dissolved, or gaseous, polymerizes into dianthracene in ultra-violet light. It was reported that, on increasing the time of illumination, a stationary state can be reached, and that the concentration of dianthracene in solution is directly proportional to the intensity of light. The amount of dianthracene decreases rapidly with increasing temperature. The same stationary state can be reached when we start with a solution of dianthracene, instead of anthracene.

Investigations revealed that the depolymerization of dianthracene is a unimolecular dark reaction having a temperature coefficient of 2.8 for a 10° rise. The velocity of polymerization in light at lower temperatures is a reaction of zero order, and is only slightly affected by temperature (temperature coefficient for a 10° rise being 1.1 in phenetole). The zero order of the photochemical reaction shows that the absorption of active light is practically complete. Luther and Weigert, placing between the reaction vessel and the light source light filters made of anthracene solutions, reported that the photochemically active ultra-violet radiation is completely absorbed by solutions of anthracene in layers only a few mm. thick. Hence the velocity of photochemical reaction is apparently proportional to the amount of light energy absorbed. The velocity of the reaction can be conveniently followed because on exposing a phenetole solution of anthracene to light dianthracene separates out.

The velocity of the photochemical reaction varies in different solvents in the following decreasing order: Benzene > toluene > xylene > anisole > phenetole. From Luther and Weigert's experiments Bodenstein calculated the quantum yield to be about unity, whilst from Weigert's later experiments the calculated quantum yield was approximately 0.3 molecule of anthracene disappearing per quantum of light

absorbed. There is a complication because under the action of ultra-violet light anthracene emits fluorescent light, and hence the quantum yield is likely to be less than unity. Its absorption spectrum was investigated by Hyatt (*Phys. Rev.* **19**, 391 (1922)), who observed prominent absorption bands having maxima at 3800, 3600, 3400, 3260 Å. All these bands lead to the photosensitivity and fluorescence of anthracene. The mechanism of the reaction can be represented as follows:



The velocity of the formation of the activated anthracene molecules will be expressed by:

$$(4) \quad + \frac{d[A']}{dt} = I_{\text{abs}} K_1$$

and their velocity of disappearance by

$$(5) \quad - \frac{d[A']}{dt} = K_2[A'] + K_3[A'][A].$$

Under constant illumination the concentration of activated molecules becomes constant:

$$+ \frac{d[A']}{dt} = - \frac{d[A']}{dt}$$

and

$$(6) \quad I_{\text{abs}} K_1 = K_2[A'] + K_3[A'][A];$$

$$[A'] = \frac{I_{\text{abs}} K_1}{K_2 + K_3[A]}.$$

The velocity of the formation of dianthracene is given by

$$(7) \quad + \frac{d[D]}{dt} = K_3[A'][A] = I_{\text{abs}} \frac{K_1 K_3 [A]}{K_3 [A] + K_2} = I_{\text{abs}} \frac{K_1 [A]}{[A] + \frac{K_2}{K_3}}.$$

When the stationary state of the reaction is attained, the velocity of photochemical formation of dianthracene must be equal to the velocity of depolymerization, and hence

$$(8) \quad + \frac{d[D]}{dt} = K_4[D]$$

and the stationary concentration of dianthracene is therefore given by

$$(9) \quad D = I_{\text{abs}} \cdot \frac{K_1}{K_4} \cdot \frac{[A]}{[A] + \frac{K_2}{K_3}}$$

The following table shows the observed values and those calculated from equation (9):

Anthracene mols per litre	0.010	0.020	0.040	0.080	0.120	0.160	0.240	0.300
<i>K</i> observed	(2.31)	2.85	3.55	4.85	5.60	5.65	5.98	5.95
<i>K</i> calculated	1.87	2.85	3.86	4.67	5.06	5.27	5.45	5.60

The increase in the constants with increase in the concentration of anthracene is due to the increase in the velocity of dianthracene formation at higher concentrations.

Now it is evident that in higher concentrations more of dianthracene is formed, because the amount of energy lost by fluorescence is less at higher concentrations and hence the amount of chemical change is greater. Perrin (*Compt. rend.* **178**, 140 (1924)), Wawiloff (*Z. Physik.* **31** 750 (1925)), and others have shown that the fluorescence intensity of fluorescent dyes dissolved in different solvents decreases markedly as their concentrations are increased. This phenomenon has been explained on the view that inelastic collisions take place between excited and normal dye molecules, and that this is markedly influenced by the nature of the solvents. Hence it can be deduced that solvents must influence the ratio of the velocity constants of the two opposing processes: the loss of activation by chemical change and the emission of energy by fluorescence. Volmer and Riggert (*Z. physik. Chem.* **100**, 502 (1922)) have studied the influence of short ultra-violet light (1800—2000 Å) on anthracene solutions in hexane. The larger energy of the quanta of this spectral region appears to be sufficient to detach an electron from the anthracene molecule and not merely to raise it to a higher quantum state. The photoelectric effect studied by Volmer and Riggert does not show the complications observed in the polymerization process, and appears to depend only on the amount of light energy absorbed.

POLYMERIZATION OF β -METHYLANTHRACENE.

Weigert and Krüger (*Z. physik. Chem.* **85**, 579 (1913)) have investigated in detail the photochemical polymerization of β -methylanthracene, which was first observed by Orndorff and Megraw (*J. Amer. Chem. Soc.*

22, 152 (1899)). The results obtained with this reaction are similar to those obtained with the dianthracene formation. The influence of temperature and solvents is much less pronounced in this reaction than in the other one. Assuming that the absorption of light is identical with both substances, Weigert and Krüger estimated that the quantum yield of the polymerization of β -methylantracene is about 25% greater than that in the case of anthracene.

CHAPTER XIV.

Photochemical Isomerism.

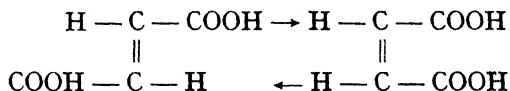
Transformation of Geometric Isomers.

It is well known that light accelerates the transformation of the Cis-form to the Trans-variety and that this phenomenon is usually reversible. Berthelot and Gaudechon (compare *Travaux scientifiques de D. Berthelot*, Paris (1917)) observed that in ultra-violet light the transformation of fumaric acid to maleic acid takes place. Kailan (*Z. physik. Chem.* **87**, 33 (1914)); *Monatsh. f. chem.* **38**, 13 (1925)) observed that the photochemical stationary state in the transformation of maleic acid to fumaric acid contains 75% of maleic and 25% of fumaric acid.

Stroemer (*Ber.* **44**, 637 (1911)) reported a similar transformation in the cases of several derivatives of coumaric and cinnamic acids, such as methylcoumaric, acetylcoumaric, methoxycinnamic acids and methylcoumarimide, methoxycinnamide, etc. These transformations are usually accompanied by polymerizations, which are not yet quantitatively investigated. Iodine and bromine act as photochemical sensitizers for most of these reactions, but do not appear to influence the equilibrium attained in the dark.

TRANSFORMATION OF MALEIC TO FUMARIC ACID.

A striking deviation from the equivalence law was observed by Warburg in the isomeric changes of maleic and fumaric acids (*Sitzb. Preuss. Akad.* 360 (1910)).



The results obtained by Warburg are as follows (p. 233).

Thus the quantum yield is much less than unity.

As a general explanation of his results, Warburg advanced the view that the molecules of both acids are decomposed into $\text{H}-\text{C}-\text{COOH}$ groups on light absorption, but that the velocity of the isomeric change

is controlled by the relative tendencies of the free groups to return to the original molecule or to form the isomer.

Conversion of fumaric into maleic acid.

Wavelength Å	Concentration of fumaric acid	Quantum yield ($\frac{\text{molecule}}{\text{quantum}}$)
2070	0.01020	0.104
	0.00306	0.080
2530	0.01020	0.0098
	0.00306	0.0087
2820	0.01020	0.134
	0.00306	0.099

Conversion of maleic into fumaric acid.

Wavelength Å	Concentration of maleic acid	Quantum yield ($\frac{\text{molecule}}{\text{quantum}}$)
2070	0.01020	0.032
	0.00514	0.037
2530	0.001020	0.043
	0.00514	0.048
2820	0.01020	0.032
	0.00514	0.035

It should be noted that the endothermic transformation fumaric \rightarrow maleic acid has a higher quantum yield than the opposite reaction.

INFLUENCE OF LIGHT ON CINNAMYLIDENE MALONIC ACID.

Bowen and collaborators (*J. Chem. Soc.* **125**, 1218 (1924)) investigated the colour change of cinnamylidene malonic acid in the crystalline state, which has a dark yellow colour and strongly absorbs radiations of wavelength 4000—5400 Å. On illumination it becomes colourless probably due to polymerization. The quantum yield for this reaction is about 0.79, which is supposed to be rather low due to the scattering of light by the fine crystals of cinnamylidene malonic acid.

TRANSFORMATION OF O-NITROBENZALDEHYDE TO O-NITROSOBENZOIC ACID.

This transformation represented by the equation: $\text{O}_2\text{NC}_6\text{H}_4\text{CHO} \rightarrow \text{ONC}_6\text{H}_4\text{COOH}$ was observed for the first time by Ciamician and Silber (*Ber.* **35**, 2040 (1901)) in presence of sunlight. This pheno-

menon was subsequently studied by Weigert and Kummerer (*Ber.* **46**, 1207 (1913)) in acetone solution illuminated by violet rays (4050 Å) and ultra-violet rays (3660 Å). The measurements of Weigert and Kummerer show that the velocity of the reaction increases a little more rapidly than the quantity of absorbed energy. For solutions, the concentrations of which were 0.1, 0.2, 0.4 and 1%, the absorption attains the values 52, 67, 89 and 99.6%, whilst the velocities for the same intensity of illumination arrange themselves in the following ratios 42, 84, 126, and 165. Recently, Weigert and Miss Brodmann (*Z. physik. Chem.* **120**, 24 (1926)), working with radiations 4360 Å, 4050 Å, and 3660 Å, and with greater care, obtained different results. The photochemical effect has now been found to be proportional to the amount of light absorbed. The quantum yield for each of these radiations is one molecule for two quanta absorbed, but the yield increases with the wavelength of the radiation when the same amount of absorbed energy is taken into account, as in the cases of the decomposition of HI and HBr. To account for this yield, Weigert and Miss Brodmann suggest that only those randomly distributed o-nitrobenzaldehyde molecules absorb radiation in which the plane of NO...CHO groups is perpendicular to the light beam and that only those molecules undergo the transformation in which the direction NO...CHO at the moment of light absorption coincides with the direction of the electric vector of the electromagnetic light waves. If this explanation be accepted, the quantum yield may be 0.5. The whole mechanism appears to be very complicated.

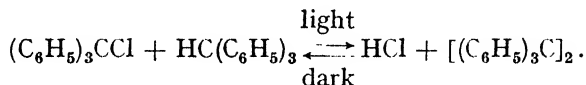
According to Bowen and collaborators (*J. Chem. Soc.* **125**, 1218 (1924)) the transformation of solid o-nitrobenzaldehyde nearly follows the law of equivalence when illuminated by radiations of wavelength (4000—4500 Å). The results seem inconclusive because of the marked scattering of the incident radiation by the crystals of the o-nitrobenzaldehyde. Berger (*Rec. trav. chim.* **44**, 49 (1925)) observed that the addition of neutral salts to aqueous acetone solutions of o-nitrobenzaldehyde caused a slight decrease of this photo-transformation.

Padoa (*Atti Accad. Lincei.* **28**, 372 (1919)) observed that the time of decomposition of single crystals of o-nitrobenzaldehyde under the action of linearly polarized light is dependent on the position of the crystal axes relative to the plane of polarization. Bowen and co-workers suggest that this phenomenon is due to the difference in the absorption coefficients of light for different planes of polarization of light, a phenomenon which is frequent in tourmaline crystals.

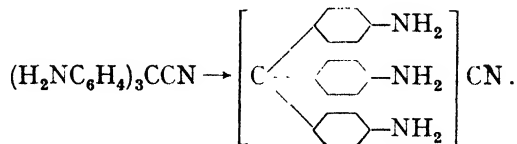
Recently, Wegscheider (*Monatsh.* **52**, 68 (1929)) has stated that the results obtained by Weigert and Miss Brodmann on the photochemical transformation of o-nitrobenzaldehyde into o-nitrosobenzoic acid are not consistent with the assumption that two quanta are used for the transformation of 1 mol of the o-nitrobenzaldehyde.

ISOMERISM OF THE TRIPHENYL METHANE COMPOUNDS.

Schlenk and Herzenstein (*Ber.* **43**, 3545 (1910)) have observed that a mixture of triphenyl methane and triphenyl chloromethane is transformed under the action of light to triphenyl methyl. The inverse reaction takes place in the dark and thus a photochemical equilibrium is established:



Lifschitz and Joffe (*Z. physik. Chem.* **97**, 426 (1921)) observed that under the influence of the near ultra-violet radiations, colourless solutions of triphenyl methane derivatives, especially leucocyanides, become coloured, and the electric conductivity of their solutions is increased. The authors advance the view that on illumination ionized salts of the dyestuff bases are formed, thus:



The salts thus formed decompose on heating, so that under illumination a stationary state is reached, the relative concentrations of the photochemical products being different with different compounds. The solvent exerts a marked influence, possibly due to the changes in the absorption spectrum of the leucocyanides. In aqueous solution the absorption in the ultra-violet is feeble, whilst in alcoholic solution it is very marked. The addition of cyanides increases the velocity of the dark reaction.

CHAPTER XV.

Allotropic Transformation of Sulphur.

Wigand (*Z. physik. Chem.* **64**, 455 (1909); **77**, 423 (1911)) observed that the mercury line 4060 Å is only slightly, and ultra-violet light completely, absorbed by soluble sulphur S_λ in its transformation into insoluble S_μ . This transformation is complicated because there is a measurable velocity of the reverse reaction in the dark, $S_\mu \rightarrow S_\lambda$, and the colloidal particles of S_μ , suspended in the solution, scatter light markedly. Only by extrapolation to the beginning of illumination is the quantitative study of the kinetics possible. The order of the reaction in its initial state in the light of a mercury lamp appears to be less than unity. The quantum yield was not measured by Wigand, but was calculated by Warburg (*Sitzb. Preuss. Akad.* **960** (1919)) to be of the order 0.07.

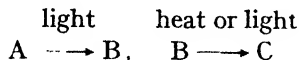
The solvent has an appreciable influence on the velocity of the reaction.

PHOTOTROPY.

Certain crystals possess the remarkable property of changing colour when exposed to light and coming back to their original colour when placed in the dark. This phenomenon has been called phototropy, and is characteristic of the crystalline state; it is doubtful whether it is a real chemical transformation.

Sometimes the reversible changes of colours observed with solutions have been included in the category of phototropy. Thus Singh (*J. Indian Chem. Soc.* **1**, 45 (1924)) has observed that a chloroform solution of α -naphthylamino camphor takes a green colour under the action of blue or violet rays and becomes colourless again in the dark. These colour changes are also accompanied by variations of rotatory power, and should undoubtedly be attributed to the formation of unstable molecular complexes. Andres has observed that a colourless solution of tetrabenzoyl ethylene $(C_6H_5CO)_2C = C(COC_6H_5)_2$ becomes yellow in light and decolorizes when the illumination is stopped. Von Halban and Geigel (*Z. physik. Chem.* **96**, 233 (1920)) have shown that no photochemical equilibrium is established, but that the reaction caused by

light is irreversible. The original substance A is first transformed in light into B, which is yellow, and which is transformed in the dark and more rapidly in light into a colourless substance C. The phenomenon is represented by the scheme:



The substance B has been isolated. It has the same molecular weight as the original substance A. Similar behaviour has been observed with other substances.

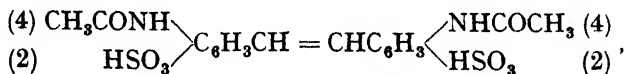
PHOTOTROPY IN CRYSTALS OF ORGANIC SUBSTANCES.

This phenomenon was observed for the first time by Marckwald (*Z. physik. Chem.* **30**, 143 (1899)) in crystals of tetrachlor- α -cetonaphthalene and of quino-quinoline hydrochloride. This latter substance forms yellow crystals which become green under the action of blue, violet or ultra-violet rays, and goes back to its original colour in the dark. This change was not observed with other salts such as the sulphate or nitrate, and hence Marckwald considered the phenomenon to be a physical one. About the same time as Marckwald, Biltz (*Lieb. Ann.* **305**, 170 (1899); *Z. physik. Chem.* **30**, 527 (1899)) made similar observations, and stated that several hydrazones and osazones take a deep colour in light which disappears in the dark. For example, crystals of benzaldehydephenylhydrazone, which are colourless, become scarlet-red and dichroic on illumination. When the crystals are dissolved in alcohol, a colourless solution is obtained.

At present, thanks to the researches of Stobbe, Padoa, Senier, and their collaborators, we know a large number of phototropic substances belonging to different classes of organic compounds, e.g. fulgides, derivatives of stilbene, salicydeneamine, etc.

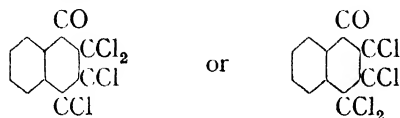
The following are some of the phototropic substances which have been carefully investigated:

Benzaldehydephenylhydrazone ($\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{NHC}_6\text{H}_5$), α -naphthyllosazone of piperile ($\text{C}_{10}\text{H}_7\text{NHN}=\text{C}(\text{C}_6\text{H}_5\text{O}_2\text{CH}_2)\text{C}(\text{C}_6\text{H}_5\text{O}_2\text{CH}_2):\text{NNHC}_{10}\text{H}_7$), α -naphthyllosazone of anisile ($\text{C}_{10}\text{H}_7\text{NHN}=\text{C}(\text{C}_6\text{H}_4\text{OCH}_3)\text{C}(\text{C}_6\text{H}_4\text{OCH}_3):\text{NNHC}_{10}\text{H}_7$), Salicydeneaniline ($\text{HOC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$), salicydene- β -naphthylamine ($\text{HOC}_6\text{H}_4\text{CH}=\text{NC}_{10}\text{H}_7$), Disalicydene m-phenylenediamine ($\text{HOC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4-\text{N}=\text{CHC}_6\text{H}_4\text{OH}$), Diacetyl diamino-p (2) stilbene — O (2) — disulphonic acid



Acetanilide-p-disulphoxide ($\text{CH}_3\text{CONHC}_6\text{H}_4\text{SO}_2\text{SC}_6\text{H}_4\text{NHCOCH}_3$). Slight changes in the composition or the chemical constitution cause the appearance or disappearance of the phototropy. Thus the osazones of anisole and of piperile are phototropic, but not those of vanillile.

Tetrachloro- α -cetonaphthalene



The phototropy of this substance has been observed by Marckwald, and its crystals, which are orthorhombic, become violet-red in light and colourless in the dark. At about 80° , the substance is transformed into a dimorphous modification. The crystals lose their transparency and phototropic properties. Weigert (*Z. Elektrochem.* **24**, 222 (1918)) has studied this substance thoroughly, and has brought to light the following facts:

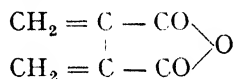
The change of colour is produced by violet or ultra-violet rays, and is not accompanied by any variation of the crystal structure or constants of the crystals. The ratio of the axes remains the same, and the X-ray radiogram is not modified. The absorption spectra of the colourless crystals, situated nearly wholly in the ultra-violet, are not the same for the polarized rays which are parallel to the vertical axis c , or in the perpendicular direction ab . Hence there is dichroism. A comparison of the absorption spectra of the crystals and their solutions in benzene or ether shows the identity of the molecules in these different states. Light has the effect of modifying the dichroism. It affects only the absorption spectrum of the rays polarized in the plane ab . An absorption band appears in the yellow-green, and this is due to phototropism. On the other hand, the effect of polarized light is more marked when the vibrations are parallel to the axis c than when parallel to the plane ab . This is unexpected, because the radiations which are most absorbed are the least active.

In most cases of phototropy, the inverse transformation is accelerated by radiations of large wavelengths. The active radiations are those which correspond to the absorption band which is formed, but these rays act only when the plane of the waves is parallel to the plane ab , and is normal, because only in these conditions are the waves absorbed. The fact that the maximum phototropic change produced by white light is obtained when the light is polarized parallel to the axis, is explained because the light thus polarized does not destroy

the coloration at the same time that it is formed. From all these facts, Weigert has drawn the conclusion that the regular orientation of the molecules in a crystal is one of the essential conditions of phototropy, which should be attributed not to a chemical transformation but to an intramolecular modification resulting from the displacement of an electron.

FULGIDES.

Fulgides, which are derivatives of the compound



in which the hydrogen atoms are replaced by aliphatic or cyclic hydrocarbon radicles, have been studied by Stobbe (*Lieb. Ann.* **359**, 1 (1907)). The derivatives containing three aryl groups are phototropic, and in light take a dark colour. This modification is temporary, but is accompanied sometimes by a durable change. According to the conditions of the experiment and the duration of illumination, one or the other phenomenon predominates.

Triphenyl fulgide has been specially studied. This substance in the powdered condition is yellow, but becomes brown under the action of blue or violet light which it absorbs. The inverse change of colour can be reproduced a large number of times by alternate light and darkness. However, it becomes less and less marked, and if the exposure to light is of a long duration the substance becomes pale, and its clear tint persists even in the dark. It appears, therefore, that along with the reversible phototropic change, there is an irreversible change. The return of the brown colour to yellow is accelerated by yellow, red, and even infra-red radiations. At the ordinary temperature, and in the dark, this reaction is slow, but it becomes more rapid when heated. Hence it can be conceived that above a certain temperature, which varies with the intensity of the light, the phototropic effect no longer occurs. The diminution of phototropic sensitivity, due to an acceleration of the inverse transformation when the temperature is elevated, seems to be general. Senier, Shephard, and Clarke have stated that certain derivatives of salicylic aldehyde remain phototropic even up to the melting point, but for others the temperature limit is lower. Salicydene-o-anisidine is phototropic up to 30°, disalicydene-m-phenylene diamine is dimorphous; one of the forms is phototropic up to 30° and the other up to 75°. Salicydene-p-anisidine, which is not

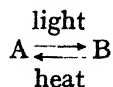
phototropic at the ordinary temperature, becomes so at -20° . This influence of temperature probably explains the observation of Padoa and Zazzaroni (*Atti Accad. Lincei*. **25**, (1), 808 (1916)) that the phototropic transformation of benziltolylsazone, under the action of relatively weak yellow light, has a thermal coefficient of less than unity.

DERIVATIVES OF STILBENE.

Certain derivatives of stilbene present a phototropy of a special kind which has been studied by Stobbe and Malisson (*Ber.* **46**, 1227 (1913)). A good deal of research has been carried out with diacetyl-p-(2) diamino-o-(2) disulphonic acid. This substance is a clear yellow powder, and becomes red when exposed to radiations of wavelengths between 4900—2700 Å. The inverse change is produced in the dark, and it is accelerated by radiations of large wavelengths. Salts of different metals (Na, K, Ba, Sr, Ca, Mg, and Pb) behave like the acid. This transformation has the remarkable peculiarity that it does not take place either in a vacuum or in hydrogen. The presence of oxygen is necessary, and there are two possibilities for explaining the influence of oxygen. The oxygen may act as a catalyst, or form an oxide or very probably an unstable peroxide. It appears more probable from the experiments of Stobbe and Malisson that an unstable peroxide is formed, because the colour change is accompanied by the production of ozone. For several compounds which have been studied, the phototropic change is not reversible, and this seems to indicate the formation of a stable product of oxidation. It appears, therefore, that the phototropy of the stilbene derivatives is of a special type and cannot be attributed to the same causes as other cases of phototropy.

OBSERVATIONS OF SENIER AND OF PADOA.

Stobbe has suggested an explanation of the phenomenon of phototropy other than those of Marckwald and of Weigert. According to Stobbe, the facts observed with fulgides can be explained if it is supposed that there are two modifications of the substance, of which A is stable in the dark and is colourless, whilst B is unstable and is formed under the action of light. B forms a solid solution with A, and in light a stationary state is produced according to the scheme:



The researches of Senier and of Padoa and their colleagues have supported the above views of Stobbe. Salicydene β -naphthylamine consists ordinarily of yellow crystals, and this is the stable form. On exposure to light the crystals become red. Senier, Shephard, and Clarke (*J. Chem. Soc.* **101**, 1950 (1912)) have been able to obtain the two varieties without the intervention of light, and using different solvents. This result was utilized by Padoa and Miss Minganti (*Atti Accad. Lincei* **22**, 500 (1913)), in measuring the velocities of the two inverse phototropic processes by comparing the colours of the exposed substances with the colours of mixtures of known composition of the two pure ingredients. They have concluded that the transformation taking place in light is unimolecular, and that for a constant light intensity the velocity

can be expressed by the formula $\frac{dx}{dt} = K(1 - x)$, where x represents the fraction of the substance transformed. The velocity of the reverse change, which takes place in the dark, is represented by the bimolecular formula — $\frac{dx}{dt} = K_1 x^2$. According to Padoa, these results indicate that the yellow form is the dipolymerized form of the red, and the two

opposed transformations can be represented as $A_2 \xrightleftharpoons[\text{heat}]{\text{light}} 2 A$. Similar

results have been obtained with benzaldehydephenylhydrazone, in which the above scheme can be applied. In this case the two varieties have not been separately isolated, but Padoa and Miss Minganti have assumed that on prolonged exposure to light the transformation of the yellow modification to red is complete.

In the case of diacetyl diamino-p'(2)-stilbene-o-(2) disulphonic acid, Padoa and Zazzaroni (*Atti Accad. Lincei* **24**, 828 (1918)) observed that the phototropic transformation is of the second order, whilst the inverse reaction is unimolecular. Padoa believes that in this case light produces

a polymerization, as in the case of anthracene: $2 A \xrightleftharpoons[\text{dark}]{\text{light}} A_2$. There

are certain objections to these views of Padoa. The application of the law of mass action to the velocities of the reactions occurring in crystals seems unsatisfactory. Moreover, cryoscopic measurements with the two varieties of salicydene β -naphthylamine in solution show that both the forms consist of simple unpolymerized molecules. Hence the two forms appear to be isomeric, and one is not a polymer of the other, as has been assumed by Padoa.

GENERAL CONSIDERATIONS.

Looking at the whole problem from a broad point of view it appears that phototropic changes involve only a slight modification of structure. Possibly a displacement of feebly bound electrons takes place, and our ordinary structural formulae do not serve to portray these slight changes. Moreover, all phototropic phenomena need not have the same characteristics, and some of them may be considered to be reversible photochemical changes, whilst others are physical transformations.

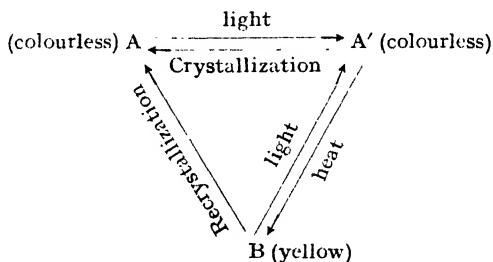
Stobbe has drawn attention to a remarkable similarity between photoluminescence and the phenomenon of phototropy. Phosphorescence is excited by radiations of short wavelength, and phosphorescent substances revert to their original condition by themselves. The velocity of the extinction of the phosphorescence is accelerated by heat or radiations of longer wavelength, and the amount of light given out during the extinction is less the greater the temperature of the medium. All these rules are applicable to phototropic transformation. Moreover, the presence of small amounts of impurity is necessary for the phenomenon of phototropy. Thus Child and Smiles (*J. Chem. Soc.* **125**, 2359 (1924); 2696, (1926)) have shown that para-disulphoxyl-acetanilide and para-disulphoxy-aniline, when carefully purified, are not phototropic, but become so when they contain small quantities (0·15%) of the corresponding disulphides. It should be emphasized that the phenomena of phosphorescence and phototropy are not associated, and Stobbe has not been successful in observing photoluminescence in the fulgides or in the phototropic derivatives of stilbene.

INVERSE PHOTOTROPY.

Heilbron and Wilson (*J. Chem. Soc.* **105**, 2892 (1914)) have observed a type of phototropy which appears to be the inverse of ordinary phototropy, first with the phenylsemicarbazone of cinnamic aldehyde ($\text{C}_6\text{H}_5\text{CH}:\text{CHCH}:\text{NNC}_6\text{H}_5\text{CONH}_2$). This substance when freshly prepared is colourless. When exposed to diffused light for a certain time no change of colour is observed, but when this exposed substance is kept in the dark, it takes up a yellow colour which disappears again in light. This inverse phototropy has also been observed by Heilbron, Hudson, and Huish (*ibid.* **123**, 2273 (1923)) in the methoxy derivatives of cinnamaldehydesemicarbazone, and in those of cinnamaldehydephenylcarbazone. The phenomenon is characteristic of the solid state, and attempts to obtain these colour changes in the dissolved condition have

been unsuccessful. The solid substance, whatever may be its condition, yields a solution of the same colour, and on crystallisation the original solid substance is obtained again. The active rays for this inverse phototropy lie in the ultra-violet. All substances which show the phenomenon of inverse phototropy are also "thermotrope". In reality they do not change colour when they are heated before they are activated by light, but after illumination even for a short time they become immediately yellow when the temperature is raised. For explaining these facts Heilbron and collaborators have proposed the following hypothesis:

The inactive and colourless molecules A absorb ultra-violet light and become active though remaining colourless. They, in their turn, can change in the dark, with greater rapidity as the temperature is increased, to another form B which is coloured. Under the action of light the molecule B can pass again to the state A' and thus photo-chemical equilibrium is produced. Heilbron has suggested the following scheme:



REVERSIBLE CHANGE OF COLOUR IN INORGANIC COMPOUNDS.

The cases of phototropy already discussed belong to complex organic compounds. However, a phenomenon recalling phototropy has also been observed in inorganic compounds. According to the experiments of Mourelle (*Compt. rend.* **158**, 122 (1914); **60**, 174 (1915)) sulphides of calcium and strontium show reversible changes of colour when they are placed alternately in the light and in the dark. These changes are produced only when these sulphides contain certain metallic salts and an excess of sulphur. These are precisely the conditions which are necessary for the phenomenon of phosphorescence with these sulphides. Hence it may be assumed that two phenomena have the same cause. Phipson (*Monde.* **53**, 353 (1880)), and Cawley (*Chem. News* **63**, 88 (1891)) have stated that a mixture of feebly calcined

barium sulphate and zinc sulphide becomes black in ultra-violet light and white again in the dark. This may be due to the formation of metallic zinc on illumination of zinc sulphide, as has been observed by Job and Emschwiller (*Compt. rend.* **177**, 313 (1923)). Similarly, chemical transformations are likely to take place in the reversible colour changes observed with cuprous chloride containing sulphurous acid on exposure to light (cf. Wöhler, *Lieb. Annal.* **130** (1874); Singh, *J. Chem. Soc.* **121**, 872 (1922)). These phenomena should not be included in the category of phototropic transformation because they appear to be really chemical.

Recently S. V. R. Rao and H. E. Watson (*J. Phys. Chem.* **32**, 1342 (1928); *J. Indian Inst. Sci.* **12A**, 1 (1929)) have prepared twenty mercury compounds of the types Hg (X) CNY and $\text{Hg X}_2 \cdot 2 \text{HgY}$ where X is chlorine, bromine, iodine, hydrosulphide, hydroselenide, thiocyanate, or selenocyanate, and Y is oxygen, sulphur, or selenium, and found them to be phototropic. By spectroscopic examination of ten of the more sensitive of these compounds it has been found that most of them are darkened by exposure to light of wavelength of the order of 5500 Å or less. A broad but well defined maximum of sensitivity is found, usually in the green, the position of which for related compounds tends to move towards the red with increase in the molecular weight of the compound. Reversal can be effected by exposure to red light in compounds previously darkened by exposure to light of shorter wavelength. For some compounds the mean temperature coefficients of the dark and light reactions were found to be 1.9 and 1.0 respectively.

Rao, Varahalu and Narasimhaswami (*Nature* **124**, 303 (1929)) have recently shown that dithiotrimercuric salts of the general formula 2HgSHgX_2 or 2HgSHgX , according as X is a negative ion of a monobasic or a dibasic acid, blacken in sunlight owing to the formation of HgS and other mercury compounds. In the dark they return to the original colour with emission of radiant energy, forming the original compound.

CHAPTER XVI.

Photosensitization.

If a system is not sensitive to light, it suffices at times to add to it a small quantity of another substance in order to make it sensitive to the action of rays absorbed by that substance. This action is known as *photochemical sensitization*, and the substance which absorbs the light and provokes the reaction without apparently taking part in it is called a *sensitizer*. There is a class of photosensitization in which a system which is chemically influenced by certain radiations is rendered sensitive to rays of another wavelength by certain substances which absorb these rays.

Several photochemical reactions have been discovered in which the light absorbing component, which is called the sensitizer, remaining itself apparently unchanged, induces change of the other substances present. These reactions, being in themselves insensitive to light of a particular spectral region, could be made sensitive to the same spectral region if a suitable sensitizer is added to the system. Two main problems are met with in dealing with photosensitized reactions, namely (1) the mechanism of the process which leads to the photosensitization and (2) the kinetics of the sensitized reactions. The photosensitizing action may be different in its nature from catalysis, as not only spontaneous reactions, but also those involving an increase in the free energy of the system can be realized by the introduction of suitable photosensitizers. The well known example of photosensitization involving an increase in the free energy of the system is the carbon assimilation process sensitized by chlorophyll.

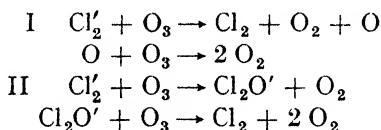
As early as 1873 Vogel (*Ber.* 6, 1305 (1873)) discovered that photographic plates could be sensitized to green and even to red light by treating them with certain colouring matters.

PHOTOSENSITIZATION BY CHLORINE.—DECOMPOSITION OF OZONE.

A good deal of research has been carried out with chlorine as a photosensitizer. A classical example of the photosensitization by chlorine is the decomposition of ozone, which possesses absorption

bands situated in the ultra-violet and in the red-yellow part of the visible spectrum. Studies of the kinetics of the photochemical decomposition of ozone indicate that the chain is dependent on the ozone concentration, and is also a function of the concentrations of other gases present in the system. Weigert (*Ann. Physik.* **24**, 243 (1907)) studied the decomposition of ozone in presence of chlorine, and observed that the rate of photosensitized ozone decomposition is entirely independent of the ozone concentration in the limits 5—0.1 per cent ozone in mixtures at atmospheric pressure. Weigert (*Z. Elektrochem.* **19**, 840 (1913)) showed later that the rate of ozone decomposition is proportional to the amount of light energy absorbed by the chlorine, and Bonhoeffer (*Z. Physik.* **13**, 94 (1923)) obtained the quantum yield 2 in mercury light of wavelength 4360 Å and 4050 Å.

The following reactions are supposed by Bonhoeffer to take place in this reaction:



Both these schemes yield two molecules of ozone per quantum of light absorbed by chlorine, if every activated chlorine molecule collides with ozone. Since the reaction velocity is independent of the ozone concentration, Bonhoeffer suggested that the life period of activated chlorine is at least 10^{-7} sec.

Schumacher and Wagner (*Z. physik. Chem. B.* **5**, 199 (1929)) have explained the chlorine sensitized decomposition of ozone by the intermediate formation of ClO. Allmand and Spinks (*Nature* **124**, 651 (1929)) have stated that the transmission for the mercury line 3650 Å of a mixture of ozone and chlorine increases appreciably during the early stages of the reaction. When gases dried with sulphuric acid are used, a distinct mist is formed on illumination. When chlorine dioxide dried by phosphorus pentoxide is mixed with dry ozone, a red liquid, which forms chloric and perchloric acids by hydrolysis, is generated. The authors have attempted to explain the above results by the formation of ClO₃ groups, ClO₂ molecules, and chlorine hexoxide, by the interaction of chlorine atoms and ozone or oxygen molecules. According to Bodenstein and Schumacher (*Z. physik. Chem. B.* **5**, 233 (1929)) the following reactions occur when a mixture of chlorine and ozone is exposed to light of such wavelengths as to be absorbed by ozone rather than by chlorine:

- (1) $O_3 + E = O_3 \text{ (activated)}$;
- (2) $O_3 \text{ (activated)} + Cl_2 = ClO + ClO_2$;
- (3) $ClO_2 + O_3 = ClO_3 + O_2$;
- (4) $ClO_3 + O_3 = ClO_2 + O_2$;
- (5a) $ClO_3 + ClO_3 = Cl_2 + 3O_2$;
- (5b) $ClO_3 + ClO_3 = Cl_2O_6$;
- (6) $ClO + ClO = Cl_2 + O_2$.

This scheme leads to the formation of one molecule of chlorine hexoxide per two quanta of light absorbed, and this is an experimental observation.

PHOTOSYNTHESIS OF WATER.

Weigert first observed that the formation of water from its elements is sensitized by chlorine. Although a mixture of pure hydrogen and oxygen combines only in the ultra-violet light, in presence of chlorine the same mixture combines in visible light. According to the experiments of Norrish and Rideal (*J. Chem. Soc.* **127**, 787 (1925)) the velocity of the formation of water is independent of the pressure of hydrogen and can be expressed by the relation

$$\frac{d[H_2O]}{dt} = K[Cl_2] \times [O_2].$$

To explain this phenomenon, Norrish and Rideal assume that the oxygen molecules are activated by the accession of energy to them from the chlorine molecules, which are activated by the absorption of light quanta. The action of chlorine in the photosynthesis of water should be studied from the point of view of the retarding influence of oxygen in the photosynthesis of hydrochloric acid, because if active chlorine can activate oxygen, then it is likely that active chlorine will not react with hydrogen.

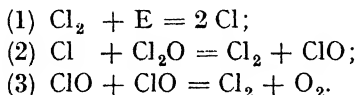
SENSITIZED DECOMPOSITION OF CHLORINE MONOXIDE.

Bodenstein and Kistiakowsky (*Z. physik. Chem.* **116**, 371 (1925)) showed that the photochemical decomposition of chlorine monoxide studied by Bowen (loc. cit.) is also photosensitized by chlorine. Chlorine monoxide has an absorption band in the same spectral region as chlorine, and the photosensitized reaction appears to be superimposed upon the unsensitized decomposition. The authors reported that the velocities of both these reactions of chlorine monoxide in radiation of wavelength 4360 Å were determined by the relative amounts of light

energy absorbed by chlorine and chlorine monoxide, and that both the reactions, independent of the chlorine monoxide concentration (94% to 0.5%) gave the quantum yield of two molecules of chlorine monoxide decomposed per quantum of light absorbed. Bodenstein and Kistiakowsky's experiments show that in the photochemical reaction a stationary concentration of chlorine dioxide is formed on irradiation. This observation leads to the conclusion that the reaction mechanism involves activated molecules.

It will be interesting to note in this connection that Bonhoeffer (loc. cit.) observed that as many as 30 ozone molecules are decomposed per quantum of light absorbed in the photosensitized decomposition of ozone in presence of bromine as sensitizer. Moreover, a mixture of chlorine and ozone when exposed to red light forms chlorine hexoxide (Cl_2O_6), whilst a mixture of ozone and bromine explodes vigorously in red light if 50—60% ozone is used.

Schumacher and Wagner (*Z. physik. Chem. B.* **5**, 199 (1929)) have advanced the view that ClO is the intermediate product in the chlorine sensitized decomposition of chlorine monoxide in radiations of 4300 Å, which are supposed to atomize a chlorine molecule. The scheme may be represented as follows:



This explains the quantum yield 2, as obtained by Bodenstein and Kistiakowsky. The quantum yield 1 obtained by Bowen (*J. Chem. Soc.* **123**, 1199 (1923)) in carbon tetrachloride solution is attributed to the removal of chlorine atoms by impurities.

Weigert (*Z. physik. Chem.* **106**, 407 (1923)), in explaining the photo-sensitization by chlorine, advanced the view that chlorine is capable of emitting the absorbed light energy in the form of isochromatic radiation, thus possessing the property of resonance fluorescence over its whole continuous absorption spectrum. According to Weigert, the emitted radiation is then absorbed by other chlorine molecules, and the process is repeated until the light quantum is absorbed by ozone molecules or by chlorine in close proximity of ozone molecules. According to this view the way in which ozone is activated on illumination by blue light in presence of chlorine must be different from the process of direct absorption of light energy by ozone molecules. Otherwise no suitable explanation can be advanced as to why the reactions caused by ultra-violet and by red light in the absence of chlorine have apparently

identical kinetics, but differ so radically from the kinetics first investigated by Weigert in the photosensitization in presence of chlorine. Another complication arises from the calculation of Weigert, namely that as many as 10^4 emission and absorption processes by chlorine must proceed the absorption of a quantum of blue light by ozone. The mechanism by which the light quantum is retained all this time in the mixture is not explained by Weigert.

Budde (*J. prakt. Chem.* **7**, 376 (1873); compare Shenstone, *J. Chem. Soc.* **71**, 471 (1897); Mellor, *J. Chem. Soc.* **81**, 1289 (1902); Bevan, *Phil. Trans.* **202**, 19 (1904)) observed an increase of pressure on illuminating chlorine by rays which are absorbed by it. More recent investigations have shown that this effect is due to the heating of chlorine by the absorbed light energy, and that in pure and dry chlorine the Budde effect is very greatly decreased. It should be noted, however, that very recently Martin, Cole and Lent (*J. Phys. Chem.* **33**, 148 (1929)) have stated that the expansion of chlorine on exposure to light does not disappear, nor is it greatly lessened, on careful purification and drying of the gas. Nor has careful baking out of the walls of the insolation bulb before admission of the dried chlorine any effect on the photo-expansion. Weigert explained these observations by suggesting that in pure chlorine the total absorbed light energy is emitted again as resonance radiation, whereas in presence of moisture a part of the radiant energy is converted into heat. Similarly Ludlam (*Proc. Roy. Soc. Edin.* **34**, 197 (1924)), and later Lewis and Rideal (*J. Chem. Soc.* **128**, 583 (1926)), observed that in absence of water vapour the Budde effect in bromine is very small, and therefore suggested the re-emission of the absorbed radiation. Lewis and Rideal reported that the intensity of the Budde effect is proportional to the concentrations of bromine and water vapour, and concluded that a hydrate $\text{Br}_2\text{H}_2\text{O}$ is formed which is the photosensitive constituent. They stated also that the absorption of light by dry bromine begins at shorter wavelengths than that by wet bromine, and ascribe the light absorption of bromine in the region 6100—5700 Å chiefly to the bromine hydrate. Recently however, Brown and Chapman (*J. Chem. Soc.* 560 (1928)) found that purified bromine, dried for several days with phosphorus pentoxide which had been freed from lower oxides, showed the same photo-expansion as ordinary somewhat moist and somewhat impure bromine. Moreover, Mathews (*Trans. Faraday Soc.* **25**, 41 (1929)) has observed a slight expansion when mixtures of dried bromine vapour and air at temperatures between 20° and 90° are illuminated by a 100 c.p. lamp. There was more expansion when the gas had not been dried. On the other

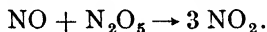
hand, the careful determination of the light absorption of dry and wet chlorine by von Halban and Siedentopf (*Z. physik. Chem.* **103**, 71 (1923)) established the fact that the light absorption in both cases is identical. Moreover, Dymond (*Z. Physik.* **34**, 553 (1925)) showed that iodine, illuminated by light of its continuous absorption spectral region does, not fluoresce at all. Kistiakowsky (*J. Amer. Chem. Soc.* **49**, 2194 (1927)) observed that the fluorescence emitted by chlorine on illumination with visible light is considerably less than 5% of the absorbed light energy. Recently, Kistiakowsky (*J. Amer. Chem. Soc.* **51**, 1395 (1929)) has shown that the Budde effect for bromine and chlorine undergoes no change when these halogens are purified and dried.

Moreover, Cole (*Trans. Ann. Electrochem. Soc.* **49**, 135 (1926)) has measured the light scattered by commercial chlorine, and also by chlorine dried by long contact with phosphorus pentoxide and has found not the slightest difference in their scattering. Indeed chlorine, wet or dry, scatters quite normally, that is, its intensity is normal as calculated from the Rayleigh formula; and this measured scattering is a thousand fold less intense than must be any hypothetical isochromatic fluorescence which would explain Shenstone's results. Nor does lowering the pressure of chlorine result in any visible fluorescence. Iodine at low pressures fluoresces brilliantly, and it is easy to observe this fluorescence, which is a thousand times more intense than the scattering. Daure (*Compt. rend.* **183**, 31 (1926)) has shown that bromine also fluoresces at low pressures (best at about 1 mm.), but the intensity is less than one per cent of that of iodine. Martin, Cole, and Lent (*J. Phys. Chem.* **33**, 149 (1929)) have concluded that dried chlorine at atmospheric pressure and at lower pressure shows no abnormal scattering, or any fluorescence which can be detected visually or photographically. It is commonly assumed that dry chlorine does not expand on insolation, but that it re-radiates the absorbed energy. The experimental results of different workers in this field seem not to be in agreement with this assumption.

Weigert and Nicolai (*Z. physik. Chem.* **131**, 267 (1928)) have studied the occurrence of isochromatic fluorescence in pure dry chlorine by means of a mercury vapour lamp. Contrary to expectation, decrease of the distance between the vessel containing chlorine and the actinometer causes the quantity of hydrogen chloride produced to diminish by about 60%. The authors could not substantiate the occurrence of fluorescence in chlorine, and thought that Lambert's law was invalid. Hence it appears that there is very little experimental support in favour of Weigert's views, and the Budde effect is only a secondary process involving small quantities of the energy absorbed.

SENSITIZED DECOMPOSITION OF NITROGEN PENTOXIDE.

Daniels and Johnston (*J. Amer. Chem. Soc.* **43**, 72 (1921)) observed that the decomposition of nitrogen pentoxide was not accelerated by visible light unless some nitrogen peroxide, which shows strong light absorption in the blue part of the visible spectrum, was present. By the use of light filters these authors were able to demonstrate that only light of wavelength shorter than 4600 Å was effective in producing decomposition. An approximate calculation of the quantum yield on the basis of the data obtained by Daniels and Johnston in wavelengths 4000—4600 Å shows that about 18 molecules of nitrogen pentoxide are decomposed in presence of nitrogen peroxide, per quantum of light absorbed. Fazel and Karrer (*J. Amer. Chem. Soc.* **48**, 2837 (1926)) suggested that on illumination by radiations of wavelength 4000 to 4600 Å the nitrogen peroxide molecules are activated, and that then they collide with nitrogen pentoxide molecules causing the decomposition of the latter. Norrish (*Nature* **119**, 123 (1926); *J. Chem. Soc.* 761 (1927)) advanced another theory of the mechanism of this photosensitization. He showed that nitrogen peroxide is dissociated into oxygen and nitric oxide on absorption of light energy, and that possibly nitrogen pentoxide is decomposed in a secondary thermal reaction with nitric oxide according to the equation:



For this mechanism to play an important part in the pentoxide decomposition, it is necessary for the thermal reaction between nitric oxide and nitrogen pentoxide to have a rate at least comparable with the rate of recombination of nitric oxide and oxygen. Busse and Daniels (*J. Amer. Chem. Soc.* **49**, 1257 (1927)), by mixing nitric oxide and nitrogen pentoxide and observing the immediate formation of the brown peroxide, have shown that this reaction is indeed very rapid.

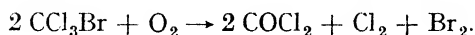
Recently, Baxter and Dickinson (*ibid.* **51**, 109 (1929)) have investigated the decomposition of gaseous nitrogen pentoxide in the presence of nitrogen peroxide in radiations of wavelengths 4350, 4050 and 3660 Å. From a comparison of the velocities of the photochemical decomposition of nitrogen pentoxide and nitrogen peroxide, it is concluded that the mechanism of this sensitized photochemical decomposition is essentially that suggested by Norrish, namely the formation of nitric oxide and oxygen from the photodecomposition of nitrogen peroxide, followed by dark reaction between nitric oxide and nitrogen pentoxide.

According to Urey, Dawsey, and Rice (*J. Amer. Chem. Soc.* **51**, 3190 (1929)), the absorption spectrum of nitrogen pentoxide shows continuous absorption commencing at 3050 Å and extending to the short ultra-violet. The long wavelength limit of this continuous spectrum closely corresponds to the energy change in the reaction $\text{N}_2\text{O}_5 = 2 \text{NO}_2 + \text{O}$, and shows that this may be the primary photochemical reaction. The authors have pointed out two possible mechanisms for the thermal decomposition of nitrogen pentoxide, and these are analogous to the radioactive decomposition of nuclei, as suggested by Gurney and Condon (*Nature* **122**, 439 (1928)), and the spontaneous dissociation of the hydrogen molecule into two normal atoms, as advocated by Blackett and Franck (*Z. Physik.* **34**, 389 (1925)) to account for the continuous hydrogen spectrum.

It is interesting to note that the Einstein law of equivalence is not applicable to this reaction, that many molecules of nitrogen pentoxide decompose per quantum of light absorbed, and that in this decomposition generation of ions has been observed by Brewer (*J. Amer. Chem. Soc.* **46**, 1403 (1924)), also compare Dhar (*Z. anorg. Chem.* **159**, 103 (1926)).

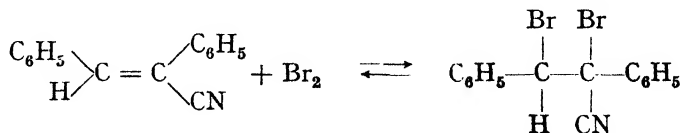
SENSITIZED OXIDATION OF CARBON TRICHLOROBROMIDE.

Grüss (*Z. Elektrochem.* **29**, 144 (1922)) observed that carbon trichlorobromide, when illuminated by visible light in presence of bromine and oxygen, becomes oxidized according to the following equation:



The velocity of this reaction is proportional to the amount of light energy absorbed by bromine. The quantum yield obtained in radiation of wavelengths 4630 and 4650 Å has a value of nearly one molecule of oxygen reacting per quantum of light energy absorbed by bromine. Grüss advanced the view that activated bromine molecules are formed as a result of light absorption, and that they can activate oxygen molecules by collisions.

Addition of Bromine to α -phenylcinnamionitrile. The reaction between bromine and α -phenylcinnamionitrile is sensitized by bromine and is reversible:



Plotnikoff (*Lehrbuch der Photochemie* 250 (1920)) investigated this reaction and showed that it is reversible. Berthoud and Nicolet (*J. Chim. phys.* **25**, 40 (1928)) investigated this reaction in detail in CCl_4 solution. The dark reaction is very slow, and under the influence of blue light the reaction takes place in both directions, and a state of equilibrium, which does not depend on the intensity of light, is attained. The following empirical relation is applicable to this equilibrium

$$\frac{[K_1 \cdot A + K_2 \text{ A Br}_2][\text{Br}_2]}{[\text{A Br}_2]} = K$$

where A = concentration of the nitrile, and A Br_2 = concentration of the dibromoderivative. The two coefficients K_1 and K_2 are of the same order of magnitude.

Experimental results show that the velocity of the formation of the bromo-derivative is independent of the concentration of the nitrile, and the velocity can be represented by the following relation:

$$v_1 = \frac{d[\text{A Br}_2]}{dt} = K I_0^{\frac{1}{2}} [\text{Br}_2],$$

when the absorption of light is complete and I_0 represents the intensity of the incident radiation. The reverse reaction takes place only in presence of bromine acting as a photosensitizer. If a solution of the pure dibromoderivative is exposed to light, at first there is very little decomposition, and later the velocity increases as the amount of bromine increases in the system. If a small quantity of bromine is added in the beginning, the induction period is decreased. This is a phenomenon of autosensitization. The velocity of decomposition of dibromocinnamonnitrile can be expressed by the following equation:

$$v_2 = - \frac{d[\text{A Br}_2]}{dt} = K_1 \frac{I_0^{\frac{1}{2}} \cdot [\text{A Br}_2]}{[\text{A}]},$$

when the absorption is complete. Consequently, the real velocity of the formation of the dibromoderivative is the difference between these two velocities.

Now, the velocity of the formation of the dibromoderivative and of its decomposition is proportional to the square root of the intensity of light, and hence it is assumed by Berthoud and Nicolet that bromine atoms take part in both the reactions. According to the above authors the atomic bromine formed as the primary product of illumination reacts on the dibromoderivative according to the following equation:

$\text{ABr}_2 + \text{Br} \rightarrow \text{Br}_2 + \text{ABr}$, where ABr is the intermediate mono-bromoderivative, which is supposed to decompose spontaneously.

TRANSFORMATION OF THE CIS FORM INTO TRANS.

Liebermann (*Ber.* **28**, 1443 (1895)) stated that a benzene solution of allofurfuracrylic acid is transformed into furfuracrylic acid very slowly in sunlight, but that a small quantity of iodine hastens the reaction greatly. The reaction takes place according to the following equation :



Liebermann also observed that the velocity of the transformation of allocinnamylidene-acetic acid ($\text{C}_6\text{H}_5\text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{COOH}$) in light is greatly accelerated by traces of iodine. Several other photo-reactions of this type have been found to be accelerated by the presence of iodine, but few quantitative results are available.

The transformation of symmetric bi-iodoethylene from the Cis-form to Trans-form takes place in the dark:



Latiers (*Bull. Soc. Chim. Belg.* **31**, 73 (1922)) observed that this transformation is accelerated by light, but that in presence of light the equilibrium is not shifted. He has observed that the velocity of both these reactions is mono-molecular and is accelerated by iodine, and that the velocity is proportional to the square root of the iodine concentration.

SENSITIZED MALEIC-FUMARIC ACID TRANSFORMATION.

Wislicenus (*Ber. Sachs. Akad. Wiss.* **47**, 491 (1895)) observed that in presence of bromine, an aqueous solution of maleic acid was rapidly converted into fumaric acid on illumination by visible light. Eggert and collaborators (*Physik. Zeit.* **25**, 19 (1924); **26**, 865 (1925); *Z. Elektrochem.* **33**, 542 (1929)) investigated this photosensitized transformation not only with acids but also with their diethyl esters. They also investigated the bromination of the double bond, and found that the transformation of diethyl maleate ester into fumarate ester is associated with the evolution of 7000 calories. Their experimental results show a quantum yield of 295 at 21° in radiation of wavelength 4630 Å in

the isomerization of diethyl maleate ester into the corresponding fumarate, and that the quantum yield of the bromination process of diethyl maleate ester under the same condition has a value of 8.2. It is rather interesting that for this reaction the quantum yield is independent of the light intensity, and hence the velocity of the reaction appears to be proportional to the light intensity. The quantum yield in radiation of wavelength 5460 Å is practically half of that obtained in 4630 Å. The temperature coefficients of the photochemical isomerization and bromination are high. The authors also investigated the action of bromine on the fumarate ester and observed only bromination and no isomerization. They stated that the kinetics of this reaction are very similar to those of the bromination of maleate ester.

✓ Eggert suggests that excited bromine molecules are primarily formed on illumination, and that they should have fairly long life periods and should be protected against the deactivating action of collisions with solvent molecules. Herzfeld pointed out that the mechanism of the process is better explained on the view of the primary formation of the activated bromine atoms on illumination. Berthoud (*Trans. Farad. Soc.* **21**, 554 (1925)) also arrived at the same conclusion, and suggested that an intermediate product having a trivalent carbon atom is formed in the process. In the additive reaction, it has been assumed that at the moment of collision between the bromine atom and the ester molecule a bromine molecule, which may collide simultaneously, will be taken up to form dibromosuccinic ester, with reliberation of the bromine atom.

4) Recently Wachholtz (*Z. physik. Chem.* **135**, 1 (1927); *Z. Elektrochem.* **33**, 545 (1927)) has developed a theory of the mechanism of these reactions, and has assumed that the bromine atoms obtained on illumination combine with the ester molecules present to yield a short-lived compound of the life period of 10^{-11} second; and this has been called a quasimolecule, which may be decomposed again under simultaneous isomerization of the ester molecule, or be transformed into a more stable compound having a trivalent carbon atom, as suggested by Berthoud. The relative velocities of both these processes depend on the statistical probabilities of the corresponding intramolecular changes. If the unstable quasimolecule collides with a bromine molecule, the diethyl ester of dibromosuccinic acid is formed, and a bromine atom is liberated again. In order to explain the high temperature coefficient of these reactions Wachholtz suggests that at about 20° a new degree of intramolecular freedom of the ester molecules comes into play and modifies the stability of the quasimolecules.

Wachholtz has obtained a quantum yield of 430 at 21° in the conversion of maleic acid into fumaric acid in presence of bromine and sulphuric acid, when the concentration of maleic acid is high. The quantum yield decreases with the decrease in the concentration of maleic acid, and becomes dependent on the light intensity. The temperature coefficient of the reaction is about 2. These facts lead to the view that bromine atoms are responsible for the conversion of maleic into fumaric acid. In the reaction $\text{Br}_2 + h\nu = 2 \text{ Br}$, every fiftieth absorbed quantum is assumed to be effective.

R. Schmidt (*Z. physik. Chem.* B. 1, 205 (1928)) has assumed that the photosensitive reaction between bromine and methyl maleate depends on the formation of bromine atoms by the action of light. The quantum yield with methyl maleate varies with the initial concentrations of ester and bromine, the intensity and wavelength of the incident light, and the temperature. The study of the addition of bromine to methyl fumarate affords values for the quantum yield which are in agreement with those expected from Wachholtz's investigation of the ethyl esters. In aqueous solution the quantum yield is approximately the same as in carbon tetrachloride solution.

ISOMERISM OF BENZOYLACRYLIC ACID DERIVATIVES.

Rice (*J. Amer. Chem. Soc.* 45, 222 (1923); 46, 214 (1924)) observed that benzene solutions of the yellow ethyl and methyl esters of benzoylacrylic acid and of paramethoxybenzoylacrylic acids are transformed in sunlight into unstable colourless isomers. In the presence of small quantities of bromine and iodine the reverse reaction takes place in sunlight. It is believed that the halogens themselves do not undergo any chemical change, and hence it is a case of pure photosensitization, but quantitative results are not yet available.

SENSITIZATION BY URANYL SALTS.

(1) DECOMPOSITION OF OXALIC ACID. — The photosensitizing action of uranyl salts has been studied by a large number of investigators since the beginning of the nineteenth century, but few quantitative results are available. Uranyl (UO_2^{++}) salts are yellowish green and fluorescent, and become reduced by oxidizable substances in presence of blue, violet, and ultra-violet light. Thus uranyl sulphate is reduced by alcohol, glycerol, lactic acid, etc. in light. In some cases with this photosensitization the uranyl ion (UO_2^{++}) is simultaneously reduced to the uranous state. The decomposition of oxalic acid in

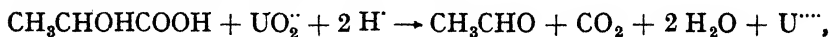
presence of uranyl salts has been largely investigated. Fay (*J. Amer. Chem. Soc.* **18**, 269 (1896)) observed that in addition to carbon dioxide, carbon monoxide and formic acid are formed in this reaction, and that the uranyl group is partly reduced to uranous ion. Berthelot and Gaudechon (*Compt. rend.* **157**, 333 (1913); **158**, 1791 (1914)) reported that no formic acid is formed in the photosensitized decomposition of oxalic acid, but Bruner and Kosak (*Z. Elektrochem.* **17**, 354 (1911)) observed formic acid amongst the products of decomposition.

The photosensitized decomposition of oxalic acid in presence of uranyl salts has also been investigated by Landau (*Compt. rend.* **156**, 1894 (1913)), Mathews and Dewey (*J. Phys. Chem.* **17**, 211 (1913)), and Holmes (*Amer. Dyestuff Rep.* **13**, 188, 197 (1924)), who has noted that the photochemical decomposition of oxalic acid sensitized by uranium salts is quantitative, and may be employed for the determination of the light-fastness of dyes. Bacon (*Filippine. J. Sci.* **2**, 129 (1907); **5**, 281 (1910)) observed that the velocity of the sensitized decomposition of oxalic acid in sunlight was completely independent of the acid concentration, and was not measurably affected by change of temperature from 20° to 100°, or by the addition of acids and bases so long as the solution remained acid. Bacon also observed that the velocity of reaction increased with the increase in the uranyl salt concentration. In neutral solution, the reaction is complicated by the formation of a precipitate containing uranium oxides. Boll (*Compt. rend.* **156**, 1891 (1913)), working with very dilute solutions of uranyl acetate in radiations of wavelength 2500 Å, observed that the rate of reaction was approximately proportional to the oxalic acid concentration, and that about 50 molecules reacted per absorbed quantum. On the other hand, recently Anderson and Robinson (*J. Amer. Chem. Soc.* **47**, 718 (1925)), working with more concentrated solutions of acetic acid and uranyl salts, obtained the yield 0.03. Bowen and Watts (*J. Chem. Soc.* **127**, 1707 (1925)), however, found one molecule of oxalic acid to be decomposed per absorbed quantum, in agreement with the measurements of Büchi (*Z. physik. Chem.* **111**, 269 (1924)) in visible light ($\lambda = 4200$ Å). Büchi observed that the velocity of the reaction was independent of the oxalic acid concentration only so long as this was in excess of the uranyl salt, and the temperature coefficient for a 10° rise was nearly unity. For lower concentrations of oxalic acid, a decrease in the velocity of the reaction was observed. Addition of an excess of sulphuric acid decreased the velocity of the reaction. Büchi observed that formic acid was formed to the extent of 40% of the decomposed oxalic acid, and that the yield of formic acid decreased in more acid solutions. He advanced

the view that in solutions of uranyl salts containing an excess of oxalic acid, practically the total amount of uranyl ion is present in the form of a complex acid ($\text{UO}_2\text{H}_2\text{C}_2\text{O}_4$), and that this is the photosensitive component, which decomposes on absorption of light quanta either by the reaction: $\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O}$, or by the reaction $\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{HCOOH} + \text{CO}_2$. The reduction of uranyl ion is likely to be due to a secondary reaction, possibly with the formic acid formed. The formation of a complex with uranyl salts and oxalic acid is supported by the observations of Henri and Landau (*Compt. rend.* **158**, 181 (1913)) on the absorption spectra in ultra-violet. A marked increase in light absorption in the region 3200—2700 Å by uranyl salts is caused by adding oxalic acid, which shows only a weak absorption in the above region. The deviations from Beer's law suggest the formation of the complex $\text{UO}_2 - \text{H}_2\text{C}_2\text{O}_4$ even in the presence of strong acids.

Recently Pierce (*J. Amer. Chem. Soc.* **51**, 2731 (1929)) has reported that the temperature coefficient of the photolysis in presence of uranyl sulphate, in the case of oxalic acid is unity, and with malonic acid 1.13. The velocity of the reaction is independent of the concentration of uranyl sulphate between the limits 0.0025 M — 0.01 M, but depends on the concentration of malonic acid. It is suggested that the reaction may be due to the decomposition of an intermediate uranyl ion-acid complex, or to inelastic collisions between activated uranyl ions and acid molecules.

(2) DECOMPOSITION OF LACTIC ACID.—Bolin (*Z. physik. Chem.* **87**, 490 (1914)) studied the decomposition of lactic acid sensitized by uranyl salts, and obtained relations similar to those with oxalic acid decomposition. The velocity of the reaction is independent of the acid concentration so long as this is in excess, and the temperature coefficient between 20° and 30° is practically unity. With the increase in the uranyl salt concentration, the velocity of reaction reaches a maximum value. The difference between the sensitized decomposition of oxalic and lactic acids lies in the fact that, in the absence of oxygen, a yield of uranous salt to the extent of only 3% has been observed by Büchi, whilst Bolin finds that under these conditions an equivalent amount of uranyl ion is reduced to the quadrivalent uranous ion in the sensitized lactic acid decomposition. At the same time, a decrease in the velocity of the reaction with time of illumination is observed. Bolin considers that the primary reaction is:



and that in presence of air or oxygen, the uranous ion is again oxidized to UO_2^{++} .

Aloy and Rodier (*Bull. Soc. Chim.* **31**, 246 (1922)) observed that under the influence of light the solutions of uranyl salts UO_2R_2 (R is a monobasic acidic radical) decompose according to the reaction:

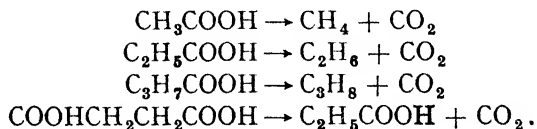
$\text{UO}_2\text{R}_2 + 2 \text{RH} + \text{A} \rightarrow \text{UR}_4 + \text{H}_2\text{O} + \text{AO}$, where A is an oxygen acceptor, e.g. ethyl alcohol, which is oxidized to acetaldehyde.

(3) FORMIC ACID DECOMPOSITION. — Hatt (*Z. physik. Chem.* **92**, 513 (1918)) observed that in the decomposition of uranyl formate solutions, the uranyl ion is reduced to uranous ion, which retards the reaction, and this retardation is attributed by Hatt to the absorption of active light by it. Hatt observed that the initial velocity of the reaction is directly proportional to the light intensity, which was varied in the ratio 1 : 280, and has reported that the quantum yield is about 0.4.

Baur (*Z. physik. Chem.* **111**, 315 (1924)) showed that as the reaction is retarded by the products of the chemical change in the initial stages of this sensitized decomposition, the quantum yield is probably near unity. This decomposition is retarded by the addition of neutral salts and acids. Hatt showed that on the addition of quinquivalent vanadium ions, instead of the reduction of uranyl ion, the quinquivalent vanadium ions were reduced to the quadrivalent condition, and when the quinquivalent vanadium was completely reduced, the reduction of uranyl ions began. On the addition of quadrivalent vanadium ions, the reaction showed a long induction period on illumination, with practically no decomposition of formic acid during this induction period.

Besides these photosensitized reactions, where the uranyl ion is reduced to the uranous state, there are some cases of photosensitization where no reduction of the uranyl ion appears to take place.

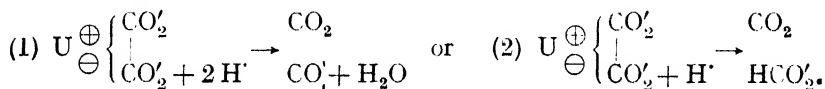
Neuberg (*Biochem. Zeit.* **13**, 305 (1908); **27**, 21 (1910); **29**, 279 (1910); **39**, 158 (1912)) observed that numerous organic substances were oxidized on illumination, by passing air in presence of uranyl salts; this also markedly sensitizes the photochemical decomposition of several organic acids. In the cases of the simple acids, only a molecule of CO_2 is given off. Thus:



Plotnikoff (*Z. wiss. Phot.* **21**, 117 (1922)) states that the polymerization of vinyl chloride, which proceeds under the action of extreme ultra-violet radiation, can be photosensitized by uranyl salts to visible light. Baur (*Helv. Chim. Acta.* **1**, 186 (1918)) reported that the photochemical

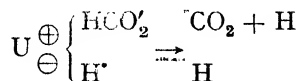
reduction of mercuric chloride by sugar was sensitized by uranyl sulphate, which appears to be unchanged. Similar results were obtained by Dhar and co-workers (*Z. anorg. Chem.* **128**, 212 (1923)). They showed that not only the photochemical decomposition of Eder's mixture, but photo-decompositions of Fehling's solution, cupriammonium oxalate, and a mixture of mercuric chloride and a soluble tartrate, are accelerated by uranyl salts.

5) Baur (*Z. Elektrochem.* **25**, 102 (1918); **27**, 72 (1921)) has developed a hypothesis explaining the action of light on uranyl salts, on the assumption that the action of light is allied to electrolysis. On absorption of light quanta, the electronic orbits of a uranyl ion are distorted, with the result that one "end" of the molecule forms a cathode, the other an anode. By the absorption of light a state of polarization is produced in which the atom (or the complex UO_2) is positive in one portion and negative in the other, and consequently becomes simultaneously oxidizing and reducing in its behaviour, according to the following scheme:



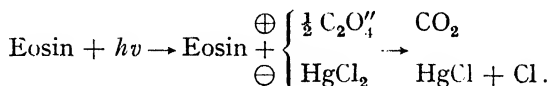
A large concentration of $\text{H} \cdot$ ions favours process (1), and this view agrees with the experimental observation that the amount of formic acid formed diminishes as the acidity increases. In neutral solution, the process (2) becomes secondary, and the reduction of the uranyl ion becomes prominent.

In the case of formic acid, the following scheme is suggested by Baur:



and the two hydrogen atoms set free reduce the hexavalent uranyl salt. This intramolecular electrolysis explains the simultaneous reducing and oxidizing action of illuminated uranyl salts on different substances. Baur is of the opinion that the experiments with mercuric chloride and sugar confirm his theory, and ascribes to sugar the rôle of a cathodic depolarizer necessary for the reduction of the mercuric chloride. Baur also asserts that the photosensitizing action of certain dyestuffs is caused by a similar primary formation of molecular cathode and anode, and the primary effect of light is always a polarization of the sensitizer; which will produce a molecular electrolysis of the acceptor acting

simultaneously as a cathodic and anodic depolarizer. The sensitizing action of eosin on the Eder mixture is represented by the following scheme:



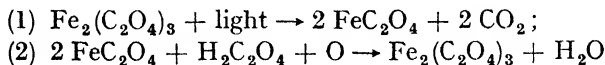
Benrath, and also Trümpler (*Z. physik. Chem.* **90**, 385 (1915)) have assumed that the photosensitization of uranyl salts is due to the alternate passage of the ion into a higher and a lower state of oxidation, as in the case of ferric salts.

SENSITIZATION BY FERRIC SALTS.

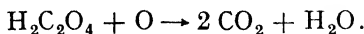
Ferric salts have marked photosensitivity. Many ferric salts, notably those of organic acids (oxalate, tartrate, citrate, etc.) decompose in light. Ordinarily the photolysis is accompanied by the reduction of ferric to ferrous ions.

On the other hand, ferric salts act as sensitizers in numerous reactions, and specially in oxidation reactions (organic acids, HI, etc.). Neuberg (*Biochem. Z.* **27**, 271 (1910)) prepared salicylic acid from benzoic acid in presence of light. Kunz, Krause, and Manicke (*Ber. pharm. Ges* **32**, 209 (1920)) have shown that oxalic acid decomposes in arc light in presence of ferric chloride.

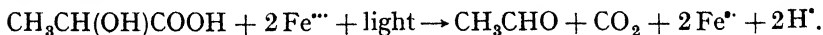
The sensitizing action of iron salts is certainly connected with their photochemical properties. Under the influence of light, the following reactions take place when air is passed through a solution of oxalic acid containing ferric salts:



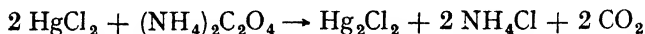
or adding up (1) and (2) we get



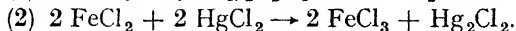
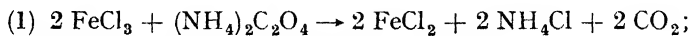
Under identical conditions, lactic acid is oxidized with the formation of acetaldehyde. The initial stage of the reaction is represented by the following equation:



In the second stage the Fe^{\bullet} ions are oxidized. Similarly, the sensitizing action of ferric salts for the Eder reaction:



can be explained from a similar point of view. Solutions of mercuric chloride and ammonium oxalate, being colourless, show marked absorption of radiations of wavelengths shorter than 3000 Å, but the Eder mixture decomposes in blue and violet rays, and this appears to be an exception to the Grotthus-Draper law. Winther (*Z. wiss. Phot.* **7**, 66, 409 (1908); **8**, 135, 197 (1910)) showed, however, that carefully purified solutions of mercuric chloride and ammonium oxalate are not sensitive to visible light, but the light sensitivity of the Eder mixture, as ordinarily observed, is due to the presence of iron salts as impurity. According to Winther, the following reactions take place in the Eder mixture in presence of iron salts:



It follows from the views of Winther that at most one molecule of calomel could be formed per quantum of light absorbed, but the quantum yield actually observed is much greater than unity. Similarly, in the oxidation of some organic acids sensitized by ferric salts, Winther and Oxholt-Howe (*Z. wiss. Phot.* **14**, 196 (1914)) obtained a quantum yield varying from 3 to 100. It is clear, therefore, that Winther's views do not lead to quantitative results.

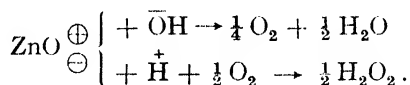
Sanyal and Dhar (*Z. anorg. Chem.* **128**, 212 (1923)) have observed that ferric salts accelerate the photochemical decompositions of Fehling's solution, ammonium and potassium cuprioxalate, and a mixture of mercuric chloride and sodium tartrate.

SENSITIZATION BY ZINC OXIDE.

Numerous reactions have been sensitized by solid zinc oxide. Eibner (*Chem. Zeit.* **753** (1911)) was the first to observe that several inorganic or organic coloured substances (e.g. Prussian blue, lead chromate, cinnabar, etc.), when mixed with zinc oxide, are reduced on exposure to light. He also observed that oil paints containing zinc oxide are more rapidly destroyed by light than those containing other inorganic substances. Winther (*Z. wiss. Phot.* **21**, 45 (1921)) studied the fluorescence of zinc oxide, and some of its photosensitizing actions. For both processes, the near ultra-violet spectral region was found to be effective. Winther showed that in presence of illuminated zinc oxide, glycerol is oxidized to glycerose, and that this reaction can be carried out either in presence of free oxygen or in presence of different inorganic compounds. In absence of air, lead carbonate is reduced to

metallic lead by the reducing action of glycerol. Winther reported that ozone is produced when zinc oxide is illuminated in presence of oxygen, but this observation needs confirmation.

Baur and Neuweiler (*Helv. Chim. Acta* **10**, 901 (1927)) have shown that by exposing aqueous suspensions of zinc oxide in contact with air to sunlight hydrogen peroxide is formed. They represent the process as follows:



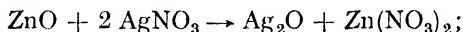
In presence of small quantities of glycerol, dextrose, or benzidine the yield of hydrogen peroxide is greatly increased; at the same time these added substances are themselves oxidized. Recently Gopala Rao, and Dhar have found that a small quantity of ozone is also formed in the absence of any added substance; and that the yield of hydrogen peroxide is increased considerably by the addition of very small quantities (about 0.01 M) of ethylamine, methylamine, aniline, phenol, acetone, alcohol, organic acids like acetic and benzoic acids, and inorganic substances like sodium hydroxide. It is interesting to note that these substances inhibit the photochemical decomposition of hydrogen peroxide (compare Anderson and Taylor, *J. Amer. Chem. Soc.* **45**, 650, 1210 (1923)). It has also been found that cadmium oxide behaves just like zinc oxide.

Recently, Böhi (*Helv. Chim. Acta* **12**, 121 (1929)) has investigated the photosensitizing action of zinc oxide on the reduction of Prussian blue, and of copper salts in presence and in absence of dextrose and glycerol. Even in presence of dextrose, the photo-reduction of Prussian blue reaches an equilibrium value of only 36%. On the other hand, in presence of glycerol or dextrose, cupric salts are photochemically reduced to the cuprous state, and finally to metallic copper. He has also studied the photo-reduction of a large number of azo-dyes by methyl alcoholic solution of chlorophyll, which is itself destroyed, but this can be prevented by adding a reducing agent like oil of turpentine, piperidine, phenylhydrazine, etc.

Böhi has also shown that by the action of light on electrolytic gas, in presence of moist zinc oxide, water and hydrogen peroxide are formed. Very recently Baur (*Helv. Chim. Acta.* **12**, 793 (1929)) has deduced certain relations regarding the kinetics of photosensitized reactions from the viewpoint of his theory (*Z. Elektrochem.* **25**, 102 (1918)). In order to explain the photosensitizing action of zinc oxide, Winther suggested that photosensitizers emit the absorbed light as

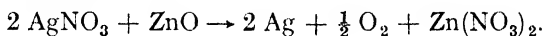
fluorescence. This secondary radiation has been assumed to be of much shorter wavelength than the absorbed light. This view is against Stokes's law of fluorescence, and with the general conceptions of the transformation of energy according to quantum principles.

Tammann (*Z. anorg. Chem.* **114**, 151 (1920)) stated that in presence of solid zinc oxide, silver oxide is deposited from a solution of silver nitrate on illumination, and zinc goes into solution according to the following scheme:

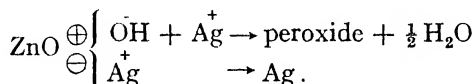


but Kohlshutter and d'Almendra (*Ber.* **54**, 1961 (1921)), demonstrated that metallic silver and not its oxide is the product of light action.

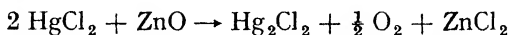
Baur and Perret (*Helv. Chim. Acta* **7**, 910 (1924)), and Perret (*J. Phys. Chem.* **23**, 97 (1926)), and Bhattacharya and Dhar (*J. Indian Chem. Soc.* **4**, 299 (1925)) also investigated the reaction. They exposed a suspension of zinc oxide or other precipitate in silver nitrate solution. Baur and Perret showed that the decomposition is due to a specific action of zinc oxide and not to the presence of any solid particle. The reaction is represented as:



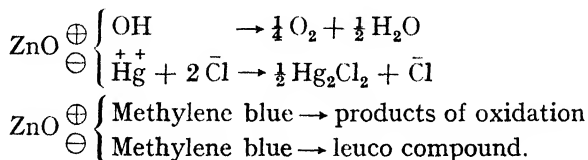
According to Baur's theory of photosensitization, the reaction follows the scheme:



Baur and Perret also studied the photosensitizing action of zinc oxide on mercuric chloride and methylene blue, and expressed their results as follows:



or



Bhattacharya and Dhar have observed that zinc oxide behaves as a very powerful sensitizer for several photochemical reactions. They have observed that the following reactions are sensitized by zinc oxide in presence of sunlight:

(1) Decomposition of Fehling's solution, (2) decomposition of cupriammonium oxalate, (3) formation of reducing sugars from formaldehyde or glycerol, (4) oxidation of methyl, ethyl, or propyl alcohol by air to the respective aldehyde, (5) formation of metallic gold from gold chloride, metallic platinum from platinic chloride, (6) oxidation of quinine sulphate by chromic acid, (7) oxidation of potassium iodide by potassium persulphate, (8) oxidation of sodium citrate by iodine, (9) oxidation of oxalic acid by iodine, (10) oxidation of potassium tartrate by iodine, (11) hydrolysis of cane sugar or maltose, (12) oxidation of sodium formate by iodine, (13) oxidation of iodoform by air, (14) oxidation of potassium tartrate by bromine, (15) oxidation of sodium nitrite by iodine, (16) oxidation of hydroxylamine hydrochloride by iodine, (17) oxidation of hydrazine hydrochloride by iodine, (18) oxidation of sodium formate by mercuric chloride, (19) oxidation of sodium sulphite by mercuric chloride, (20) oxidation of hydrazine hydrochloride by mercuric chloride, (21) oxidation of ammonium oxalate by mercuric chloride, (22) oxidation of potassium tartrate or citrate by mercuric chloride, (23) oxidation of sodium malate or lactate or dichloracetate by mercuric chloride, (24) decomposition of mercuric oxide or aqueous solutions of potassium permanganate or persulphate or oxalate.

Bhattacharya and Dhar also investigated the bleaching of numerous fluorescent and nonfluorescent dyes due to oxidation by oxygen of air, and found that zinc oxide markedly accelerates the bleaching of dyes in air. As a general behaviour it was found that the dyes which absorb light of longer wavelengths, and are of the type blue, green, or violet, are much accelerated in their bleaching in sunlight in presence of zinc oxide. Next in order come the fluorescent dyes, which also absorb light of longer wavelengths, and lastly the dyes of red, orange, and yellow colours, which absorb light of shorter wavelengths.

The following photochemical reactions are also sensitized by substances other than zinc oxide, but in all the reactions zinc oxide is the best sensitizer:

(1) Oxidation of potassium tartrate by mercuric chloride is also sensitized by ferric and ferrous chlorides, uranyl nitrate, aluminium oxide, and potassium permanganate.

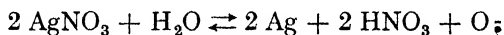
(2) Oxidation of sodium formate by mercuric chloride is also sensitized by aluminium oxide and manganese dioxide.

(3) Oxidation of ammonium malonate by mercuric chloride is also sensitized by aluminium oxide.

(4) Oxidation of sodium malate by mercuric chloride is also sensitized by aluminium oxide.

(5) Oxidation of hydrazine hydrochloride by mercuric chloride is also sensitized by aluminium oxide and erythrosin.

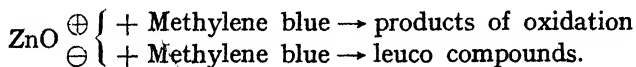
The scheme of the mechanism of photo-sensitization, as advanced by Baur, has already been discussed, but we are of the opinion that his views are unsatisfactory, because there is no experimental evidence in their support, and the decomposition of silver nitrate in presence of zinc oxide, for example, can be easily understood from the following considerations: It is well known that salts of heavy metals like silver, gold, platinum, etc. have a tendency to decompose, and in presence of light, solutions of these salts decompose readily. In presence of zinc oxide this decomposition tendency of silver nitrate is increased. In presence of light the molecules of zinc oxide absorb the incident radiation and become activated. These activated molecules come in contact with the molecules of silver nitrate and activate them by the transference of their energy. The decomposition of silver nitrate then takes place according to the following equation:



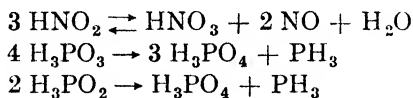
In addition to the sensitizing effect, zinc oxide has also the function of neutralizing the nitric acid which is set free, and thus helps the decomposition of silver nitrate. We have observed that in presence of calcium carbonate, strontium carbonate, etc. which also neutralize the free acid, solutions of silver nitrate appreciably decompose in sunlight, but the effect of calcium or strontium carbonate is not as great as that of zinc oxide, which also acts as a marked photosensitizer.

Chakravarti and Dhar (*Z. anorg. Chem.* **142**, 299 (1925)) have shown that solutions of dyes are unstable in presence of light, and that they can be readily oxidized or reduced under suitable conditions. Moreover, several of these dye solutions have been found to decompose in absence of air in strong ultra-violet light or sunlight, just as solutions of potassium permanganate, potassium persulphate, or ammonium nitrite decompose in presence of strong light. Bhattacharya and Dhar have shown that the decomposition of potassium permanganate, potassium persulphate, etc. in sunlight is accelerated by zinc oxide.

Baur has represented the photolysis of methylene blue in presence of zinc oxide when air is not present in the following way:



We are, however, of the opinion that these dyes, which are unstable substances, decompose in sunlight in the same way as the solution of potassium permanganate does. It is likely that the decomposition of dyes can in some cases be compared to the decomposition of nitrous acid, hypophosphorous acid, phosphorous acid, etc. according to the following equations:



SENSITIZATION BY COLOURING MATTERS.

It is well known that silver bromide paper is sensitized by different colouring matters. Several other reactions have been investigated from this point of view. Thus Pinnow (*Ber.* **34**, 2828 (1901)), and Gomberg (*Ber.* **35**, 1333 (1902)) observed that the oxidation of hydriodic acid is accelerated by fluorescein, quinine, acridine, etc. Gros (*Z. physik. Chem.* **37**, 157 (1901)) observed that the velocity of photochemical oxidation of colourless leuco bases of some derivatives of fluorescein is an autocatalytic reaction, and that its velocity can be markedly increased by the addition of some other dyestuff of the same group. Gros showed that this reaction is due to absorption of light by the dyestuff added. He further observed that by increasing the concentration of photosensitizing dyestuff, a maximum of the reaction velocity is obtained, and that a further increase of dyestuff concentration retarded the rate of reaction. According to Gros, the Eder reaction is accelerated mostly by dyes of the fluorescein group. Tappeiner and Iodlbauer (*Ber.* **38**, 2607 (1905)) showed that many inorganic and organic reactions can be photosensitized by different dyes to visible light. They stated that different substances which are equally fluorescent, such as 2—7-anthraquinone disulphonate of sodium, acridine chloride, quinine hydrochloride, are also equally effective in photosensitizing the Eder reaction.

Eder (*Phot. Korr.* **56**, 140 (1919)) has observed that the leucobases of brilliant green, malachite green, crystal violet, rhodamine B, 3 B and 6 G and leucaniline, when mixed with collodion, are more sensitive than the dyed silver bromide and silver chloride films used in photometry. The leucobase of brilliant green is specially suited for use in plant physiology experiments, being sensitive to that part of the spectrum which is active in chlorophyll formation. According to Lifschitz (*Ber.* **52**, 1919 (1919)) the colourless derivative obtained by the action of potassium cyanide on triphenyl methane dyes becomes coloured

when exposed to ultra-violet light, but slowly passes to the colourless product when kept in the dark.

Winther and Oxholt-Howe (*Z. wiss. Phot.* **13**, 89 (1914)) reported that the marked sensitizing action of eosin on a mixture of mercuric chloride and ammonium oxalate stops even before the reaction is complete, because a negative catalyst is generated in the system. This phenomenon was observed by the above authors only in visible light and not in ultra-violet radiations.

The sensitizing action of colouring matters has been supposed to be due to the formation of an unstable compound of the colouring matter with the reacting substance, which decomposes under the action of light in collision with other molecules, and in this process the sensitizer is regenerated. This view has very little experimental support.

The rôle of ordinary photosensitizers has now been explained from the theory of the interchange of energy between freely moving electrons and atoms by inelastic collision, first propounded by Klein and Roseland (*Z. Physik.* **4**, 46 (1921)), and further developed by Franck and his collaborators (*ibid.* **4**, 89 (1921); **9**, 259 (1922)).

Recently K. Burgherr (*Z. wiss. Phot.* **24**, 393 (1927)) has studied the sensitizing action of rhodamine B, eosin, and other dyes on the photo-reduction of silver nitrate by sucrose, glycine, glycerol, etc. The investigation is assumed to lend support to the theory of inner polarization mechanism for sensitization, as suggested by Baur.

Ghosh and Mitra (*J. Indian Chem. Soc.* **4**, 353 (1927)) have shown that the extinction coefficients of uranyl nitrate and varying concentrations of formic, acetic, propionic, oxalic, malonic, succinic, glycollic, lactic, tartaric, and mandelic acids are greater than the sum of those of uranyl nitrate and the organic acid taken separately. A similar rise in the extinction coefficient when ferric chloride is mixed with various organic acids has been observed by Ghosh and Mitra (*J. Indian Chem. Soc.* **5**, 191 (1928)). They assume that intermediate complexes of the organic acids and ferric chloride are formed, and that the extinction coefficients of these complexes are greater than the sum of the extinction coefficients of the respective organic acid and ferric chloride. Ghosh and Rangacharya (*J. Indian Chem. Soc.* **5**, 569 (1928)) have obtained evidence in favour of the formation of unstable intermediate complexes between mercuric chloride and various organic acids, from extinction coefficient measurements.

Bäckström (*J. Amer. Chem. Soc.* **49**, 1460 (1927)) has reported that benzophenone and acetophenone act as sensitizers for the photo-chemical oxidation of benzaldehyde and heptaldehyde.

In order to throw light on the mechanism of photosensitization, Mukerji and Dhar (*J. Indian Chem. Soc.* **5**, 411 (1928)) have photographed by the use of a quartz spectrograph the absorption spectra of several mixtures containing uranyl nitrate and ferric chloride as photocatalysts. The photographs show that in presence of uranium and iron salts, there is marked increase of light absorption, and these two substances are well known for their photosensitizing power. The addition of manganous sulphate to a mixture of oxalic and chromic acids markedly increases the absorption of light by the mixture, and Dhar (*J. Chem. Soc.* **111**, 707 (1917)) has shown that manganous sulphate is a marked positive catalyst for the above reaction. On the other hand, manganous sulphate acts as a negative catalyst in the reaction between formic and chromic acids, and it does not cause an increase of the absorption of light when added to the mixture.

Hydroquinone and phenol when added to benzaldehyde retard its oxidation, and do not increase the light absorption. Hence it appears that photosensitivity and increase of light absorption are closely associated.

PHOTOSENSITIZATION BY MERCURY VAPOUR.

Cario and Franck (*Z. Physik.* **10**, 185 (1922)), by studying the action on hydrogen gas of activated mercury vapour produced by illumination with radiations of wavelength 2536.7 \AA , observed a gradual removal of hydrogen from the gas phase. Apparently, a marked adsorption of the hydrogen on the walls of the vessel took place.

On submitting a mixture of mercury vapour and hydrogen to the action of radiations of wavelength 2536.7 \AA , which are absorbed by mercury but not by hydrogen, Cario and Franck (*Z. Physik.* **12**, 162 (1922)); **17**, 202 (1923)) have found that hydrogen gas is activated and becomes capable of reducing cupric oxide or tungstic oxide at the ordinary temperature, and a more rapid decrease of pressure was observed than in the absence of these metallic oxides. Langmuir previously showed (*J. Amer. Chem. Soc.* **34**, 860, 1310 (1912); **35**, 105 (1912); **36**, 1708 (1914); **37**, 417, 1139 (1915); **38**, 1145 (1916)) that the reduction of the metallic oxides and a marked adsorption on the walls of the vessel are characteristic of atomic hydrogen produced thermally. Franck (*Z. Physik.* **9**, 259 (1922)) elaborated Klein and Rosseland's (*ibid.* **4**, 46 (1921)) theory of inelastic collisions between atoms and electrons, and extended it to collisions between atoms and molecules, and so explained the above processes. Fuller knowledge of the

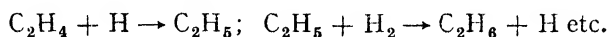
processes involved in the collisions of the second kind can be obtained from the investigations of Cario (*Z. Physik.* **10**, 185 (1922)) and Cario and Franck (*ibid.* **17**, 202 (1923)). These authors have shown that when a mixture of mercury and thallium vapours is illuminated by the line 2536.7 Å, which is absorbed only by mercury, fluorescent light is emitted by thallium as well. However, only those lines of thallium were observed the quantum energy of which is less than 112,000 calories, corresponding to the mercury line 2536.7 Å. (Cario and Franck suggested that in presence of hydrogen and excited mercury atoms, dissociation of hydrogen into atoms took place on collision with excited mercury atoms. Since the heat of dissociation of hydrogen is about 101,000 calories, the quantum energy of excited mercury atoms (112,000 calories) is sufficient to atomize a molecule of hydrogen.) The formation of hydrogen atoms by excited mercury atoms was also shown by Senftleben (*Z. Physik.* **33**, 871 (1925)), who observed that the heat conductivity of a mixture of hydrogen and mercury vapour was increased on illumination by light of 2536.7 Å. This effect cannot be ascribed to activated molecules of hydrogen.

In this connection it will be of interest to note that Taylor and Bates (*Nature*, April 19, 1930) have stated that the products of the photodecomposition of molecules showing diffuse band absorption spectra (predissociation spectra) where, according to Bonhoeffer and Farkas (*Z. physik. Chem.* **134**, 337 (1928)), the light produces dissociation by internal energy exchange, without collision, can be studied with ammonia. If ammonia at low pressures is introduced into a quartz tube containing yellow tungstic oxide, and the gas is irradiated with a hot mercury vapour arc, reduction of the yellow tungstic oxide to the blue oxide takes place in a few minutes. This appears to be due to the formation of atomic hydrogen.

Mixtures of ammonia gas, hydrogen, and carbon monoxide, when streamed through a quartz tube and illuminated by mercury arc, form formaldehyde and hexamethylene tetramine. This method of producing atomic hydrogen, by irradiating ammonia and other molecules showing diffuse spectra, is suitable for the study of reactions induced by introducing atomic hydrogen into gas mixtures.

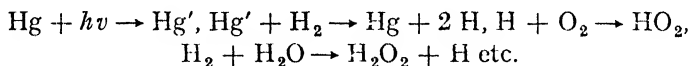
Hydrogen activated by illuminated mercury vapour can enter into reactions with different substances. Thus Dickinson (*Proc. Nat. Acad. Sci.* **10**, 409 (1924)) and Mitchell (*ibid.* **11**, 458 (1925)) showed that hydrogen thus activated combines with oxygen, forming water, and this observation has been confirmed by Taylor and Marshall (*J. Phys. Chem.* **29**, 1140 (1925)) who studied the action of activated hydrogen

on ethylene, carbon monoxide, and nitrous oxide. With ethylene, ethane is formed, with carbon monoxide different products, among which formaldehyde and methane are identified. According to Compton and Duffendack (*Phys. Rev.* **23**, 583 (1924)) nitrogen molecules are dissociated into atoms in presence of excited mercury atoms, but the effect is less marked than that with hydrogen. W. A. Noyes, Jr. (*J. Amer. Chem. Soc.* **47**, 1003 (1925)) seems to have obtained traces of ammonia by the reaction of hydrogen and nitrogen in presence of activated mercury atoms. (Cario and Franck (loc. cit.) suggested that a chain mechanism takes place in the reaction of hydrogen atoms with metallic oxides, and Taylor (*Trans. Farad. Soc.* **21**, 56 (1925)) came to the same conclusion on consideration of the absorbed quanta and the number of molecules reacting and the high quantum yield, and stated that in the case of the reaction of activated hydrogen with ethylene, the chain is likely to be as follows:



Marshall (*J. Phys. Chem.* **30**, 34, 1078 (1926)) showed that in the reaction of activated hydrogen and molecular oxygen only hydrogen is activated by collisions with excited mercury atoms, and that the rate of reaction is practically independent of the temperature.

Taylor advanced the view that the following reactions take place on illumination of a mixture of hydrogen and oxygen containing mercury vapour:



This suggestion indicates the formation of hydrogen peroxide as a primary product, from which water is formed as a product of the secondary decomposition. Marshall (*J. Amer. Chem. Soc.* **49**, 2763 (1927), compare Taylor **48**, 2840 (1926)) obtained a 100 % yield of hydrogen peroxide by passing a rapid stream of hydrogen and oxygen containing mercury vapour through the illuminated reaction vessel, there being a quantum yield of 4 molecules of hydrogen peroxide per excited mercury atom. The rate of hydrogen peroxide formation is proportional to the concentration of hydrogen present, and also to the arc current and probably to the light intensity. At high mercury vapour concentrations large quantities of mercuric oxide are formed, and the yield of hydrogen peroxide is correspondingly low. The optimum vapour pressure of mercury is 0.005 mm. The optimum concentration of mercury vapour in the lamp for obtaining the maximum amount of

resonance light (2536.7 Å) is 0.01 mm. The temperature coefficient of the photosensitized formation of hydrogen peroxide is 1.04. Bonhoeffer (*Z. Elektrochem.* **31**, 521 (1925)) obtained results similar to those of Marshall with atomic hydrogen, prepared according to Wood's method by passing a high tension electric discharge through hydrogen at low pressure. Olsen and Meyer (*J. Amer. Chem. Soc.* **48**, 389 (1926)) showed that the velocity of the reaction between hydrogen and ethylene in presence of excited mercury vapour is proportional to the square root of the hydrogen concentration. This is ascribed to the generation of hydrogen atoms in this process. In all these cases, the photosensitizing action of excited mercury vapour is practically due to the formation of active hydrogen, probably mainly atomic in nature. Results obtained with other gases will now be recorded.

Dickinson and Sherrill (*Proc. Nat. Acad. Sci.* **12**, 175 (1926)) observed that ozone is formed if a mixture of oxygen and mercury vapour is exposed to radiations of wavelength 2536.7 Å. Dickinson and Sherrill advance the view that, since the quantum of energy of an excited mercury atom is insufficient for the dissociation of oxygen into atoms, excited molecules are likely to be formed and react with normal oxygen molecules to form ozone. This reaction, and that of hydrogen peroxide formation, are complicated by the simultaneous formation of mercuric oxide.

Senftleben and Rehren (*Z. Physik.* **37**, 529 (1926)) obtained only hydrogen as the gaseous decomposition product in the photosensitized decomposition of water vapour in presence of mercury, and suggested that the reaction proceeds in the following steps:



The assumption has been made that the energy of an O—H linking is less than the excitation energy of mercury vapour, namely 112,000 calories.

Recently, Taylor and Bates (*J. Amer. Chem. Soc.* **49**, 2438 (1927)) have shown that several photochemical reactions can take place by the action of excited mercury atoms. In the following table some of the results obtained by Taylor and Bates are recorded (see p. 273). Taylor and Bates suggest that the mechanism of these reactions consists generally in an initial breaking up of one of the linkings, C—H, O—H, N—H on collision with excited mercury vapour, and hence that all these linkings possess less energy than 112,000 cal. In the decomposition of ammonia the authors find traces of hydrazine, showing

that probably NH_3 is first decomposed into H and NH_2 , and the groups NH_2 combine to form N_2H_4 .

Substance	Ratio of photo-sensitized to non-photosensitized rate of reaction	Analysis of the gaseous products of the photosensitized reaction
H_2O	—	73% H_2 ; 27% O_2
NH_3	200 : 1	89% H_2 ; 11% N_2
C_2H_4	—	88% H_2 ; 12% CH_4
CH_3OH	600 : 1	58% H_2 ; 42% $\text{CH}_4 + \text{CO}$
$\text{C}_2\text{H}_5\text{OH}$	50 : 1	46% H_2 ; 50% $\text{CO} + \text{CH}_4$
C_6H_{14}	1000 : 1	96% H_2 ; 4% CH_4
C_8H_8	30 : 1	60% H_2 ; 40% CH_4
$(\text{CH}_3)_2\text{CO}$	2 : 1	100% $\text{CO} + \text{CH}_4$
HCOOH	400 : 1	76% CO ; 24% H_2
$\text{C}_2\text{H}_5\text{NH}_2$	60 : 1	96% H_2 ; 3.7% CH_4 ; 0.3% N

Bates and Taylor (*J. Amer. Chem. Soc.* **50**, 771 (1928)) have described a cadmium lamp similar to the quartz mercury arc-lamp. Ammonia and probably hydrogen are unaffected by action of cadmium atoms in the 2^3P_1 state at 255° , but ethylene is polymerized, in complete agreement with theoretical considerations.

Recently, Taylor and Hill (*Z. physik. Chem. B.* **2**, 449 (1929)); *J. Amer. Chem. Soc.* **51**, 2922 (1929)) have shown that ethylene with an excess of hydrogen and in the presence of excited mercury atoms forms mainly ethane. If, however, relatively high concentrations of ethylene are used, the saturated hydrocarbons formed are more complex. The reaction may also form liquid condensation products of the composition $(\text{CH}_2)_n$. Methane is also formed, and appears to be unaffected by hydrogen atoms or excited mercury atoms. The effect of atomic hydrogen on the saturated hydrocarbons varies with the molecular weight of the hydrocarbon, being more rapid the greater the molecular weight. The velocity of the reaction between ethylene and hydrogen is accelerated considerably by increase in the hydrogen atom concentration, other things being equal. With large excess of ethylene, acetylene is formed in considerable quantity, but with excess of hydrogen no acetylene is formed. Hydrogen in large quantities seems to exert an inhibiting effect. The velocity of the reaction between ethylene and hydrogen in presence of excited mercury vapour depends on both the temperature and the composition of the gas. The results obtained by Taylor and Hill are not in complete agreement with those

of Bonhoeffer and Harteck (*Z. physik. Chem.* **139**, 64 (1928)), which could, however, be repeated at low pressures and with excess of hydrogen. The pressures used in the experiments of Taylor and Hill were up to one atmosphere, and under these conditions all possible kinds of reaction-products are formed.

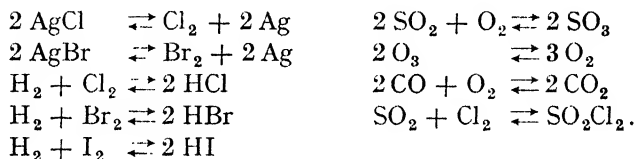
Frankenburger and Zell (*Z. physik. Chem. B.* **2**, 395 (1929)) have exposed a mixture of pentane vapour with air, nitrogen, or carbon dioxide and mercury vapour at 50° to the ultra-violet radiations from a mercury vapour lamp. The products formed varied with the nature of the gas mixed with pentane. With air a certain amount of hydrogen peroxide and aldehyde was formed. With nitrogen, some higher hydrocarbons were produced, and with carbon dioxide the resulting mixture gave the aldehyde reactions. The primary reaction in all these cases can be traced to the breaking of a C—C or a C—H linking. The final products are the results of secondary reactions.

CHAPTER XVII.

The Action of Light on diverse Inorganic Compounds.

In this and the next chapter we shall consider those photochemical reactions, which have not yet been fully investigated, and which do not easily lend themselves to suitable classification.

The following reversible photochemical reactions have been fairly fully investigated:



In most of these cases both the opposing reactions are accelerated by light, but are not sensitive to the same radiations. The result is that under different experimental conditions the reactions may be complete or attain a stationary state. Thus a mixture of H_2 and Cl_2 is completely changed to HCl in visible radiation, but in presence of ultra-violet radiation the reaction is incomplete.

The active wavelength of light necessary for the chemical change depends on the energy required for activating the molecules, and is usually different in the two opposing reactions. Moreover, the wavelength of the light required also depends upon the absorption spectra of the reacting substances. Thus in the formation of HCl or HBr , visible light is absorbed by chlorine or bromine, and thus the chemical reaction is started; whilst in the decomposition of HCl or HBr , visible radiation is not effective because it is not absorbed by HCl or HBr . In the following table the amounts of HCl , HBr , and HI formed and decomposed are recorded:

	$\lambda > 2200 \text{ \AA}$		$\lambda > 2500 \text{ \AA}$		$\lambda > 3000 \text{ \AA}$	
	Decomposition	Formation	Decomposition	Formation	Decomposition	Formation
HCl	0.42%	99.58%	0%	100%	0%	100%
HBr	100 %	0 %	20%	80%	0%	100%
HI	92.3 %	7.7 %	100%	0%	100%	0%

Hence the stability of these hydrogen compounds with respect to light decreases as the atomic weight of the halogen increases. Hydrogen chloride requires ultra-violet light of wavelength 2000 Å for decomposition, which is even then slow, while under similar conditions hydrogen bromide is rapidly and completely decomposed. Hydrogen iodide is decomposed by blue and violet light. A similar relationship has been observed by Berthelot and Gaudechon (*Compt. rend.* **156**, 889 (1913)) in the case of water vapour, hydrogen sulphide, selenide, and telluride.

Recently, Schultz (*J. Chim. phys.* **26**, 506 (1929)) has studied the decomposition of gaseous hydrogen chloride, which shows an absorption band beginning at about 2200 Å, in radiations from a very strong condensed spark between zinc or aluminium electrodes. The chlorine produced by the photochemical decomposition of HCl was so dry that it did not act on KOH or Hg. Only the ultra-violet radiations absorbed by HCl effect its decomposition. The velocity of the reaction increases, whilst percentage decomposition decreases, with increased pressure. A preliminary estimate shows that when acted upon by radiations filtered by quartz, not more than 5 mols of HCl are decomposed per quantum.

The light which passes through quartz accelerates the formation of SO₃, and starts its decomposition. Coehn and Becker (*Z. Elektrochem.* **13**, 545 (1907); *Z. physik. Chem.* **70**, 88 (1910)) studied this reaction and obtained the following relation in presence of light with different amounts of gaseous mixture:

$$\frac{[\text{SO}_2]^2 \times [\text{O}_2]}{[\text{SO}_3]^2} = K.$$

This equality is precisely the same as is predicted by the law of mass action. It is probably an accidental coincidence. Moreover, the experimental results of Coehn and Becker show that the values of "K" are not quite constant, and it seems that light does not accelerate the opposing reactions in the same ratio. Below 450°, SO₃ does not appreciably decompose in the dark, whilst Coehn and Becker working at 160° obtained a decomposition of SO₃ to the extent of 35% in light. The constant K is nearly independent of temperature (between 50° and 160°), and increases with the intensity of light. It is not clear whether the active radiations necessary for the opposing reactions are different.

The formation and decomposition of ozone constitutes the case of a typical reversible photochemical reaction, which has been extensively investigated. The active rays in the decomposition of ozone corre-

spond to the two absorption bands of ozone, one situated in the ultra-violet near 2600 Å and the other in the red region (6400 Å). The rays necessary for ozonization correspond to the absorption spectrum of oxygen extending from 1950 Å under atmospheric pressure to 2800 Å under high pressure. The ozonization always leads to a stationary state, because the active rays which cause ozonization also accelerate the decomposition of ozone, which also takes place in the dark. On the contrary, the photo-decomposition of ozone by large wavelengths is complete.

Ultra-violet light causes the decomposition of water into its elements, and also starts the formation of water from hydrogen and oxygen. In spite of a large amount of research on this reaction, the mechanism is still incompletely known. According to Tian (*Compt. rend.* **152**, 1012 (1911); **156**, 1063 (1913)) the photochemical decomposition of water is produced only by extreme ultra-violet radiations, which pass through quartz. Coehn and Grote (*Nernst-Festschrift*, Halle, 136 (1912)) observed that a stationary state is reached between water and its elements by the action of ultra-violet light. The amount of water decomposed increases with the light intensity, but it does not exceed 0.20 %, and is nearly independent of temperature. The photosynthesis of water appears to be unimolecular, and a small quantity of H_2O_2 is also formed. It is probable that oxygen is the photosensitive substance, because hydrogen at the ordinary temperature does not absorb the radiations which traverse quartz. It seems that oxygen is first atomized under the action of light, and the following secondary reactions then take place:

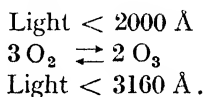
- (1) $\text{H}_2 + \text{O} \rightarrow \text{H}_2\text{O}$;
- (2) $\text{O} + \text{O}_2 \rightarrow \text{O}_3$;
- (3) $\text{H}_2 + \text{O}_3 \rightarrow \text{H}_2\text{O} + \text{O}_2$;
- (4) $\text{H}_2\text{O} + \text{O} \rightarrow \text{H}_2\text{O}_2$.

It frequently happens that products formed by the rays shorter than 2200 Å are decomposed by longer wavelengths, both ozone and hydrogen peroxide being good examples of this phenomenon. Hydrogen peroxide can only be formed by rays shorter than 1900 Å, and in order to secure a satisfactory yield the solution should be protected from light of longer wavelengths.

Wulf (*J. Amer. Chem. Soc.* **50**, 2596 (1928)) has advanced the view that O_4 is the absorbing molecule in the photochemical ozonization of oxygen at 2530 Å and 2070 Å. From Warburg's absorption data (*Sitz. Akad. Wiss.* **230** (1915)), and assuming the absorption to be proportional

to the number of O_4 molecules present, the equilibrium constant $\frac{P_{O_2}^2}{P_{O_4}}$ is calculated to be 1.2 gram/c.c.

It is well known that the air in the neighbourhood of a new quartz mercury lamp smells of ozone. When the quartz mercury vapour lamp has been used for some time the amount of ozone formation decreases, because of a pronounced decrease in the transparency of quartz in the "aged" mercury lamp to very short radiations. Lenard (*Ann. Physik.* **1**, 486 (1900)) has shown that the formation of ozone from oxygen requires radiations shorter than 2000 Å. Warburg and Regener (*Sitzungsber. K. Akad. Wiss.* 1128 (1904)) have observed that ozone may decompose in the silent electric discharge. The oxygen-ozone equilibrium may be expressed by the equation:



Potter (*U. S. Patent* 854965, May 28 (1907)), Fischer and Braehmer (*Ber.* **38**, 2633 (1905)), and others have described methods of preparing ozone by the action of light. A quartz mercury lamp is enclosed by a double walled sleeve, and a current of air is passed between the lamp and the inner wall, and a current of water through the annular space. The inner wall of the apparatus is silvered.

Baskerville (*Electrochem. and Met. Ind.* **4**, 435 (1906)), Henriet and Bonyssy (*Compt. rend.* **146**, 977 (1908)), and Fabry and Buisson (*ibid.* **156**, 782 (1913)) have studied the problem of ozone formation by sunlight. Fabry and Buisson have concluded that the ozone content of the atmosphere, if evenly distributed, would be equal to 0.6 cubic centimetre per cubic metre of air. According to Goldstein (*Ber.* **36**, 3042 (1903)) ozone is formed in the atmosphere surrounding an exhausted quartz tube through which a discharge from an induction coil is passed. Bancroft (*J. Phys. Chem.* **16**, 556 (1912)) has stated that hydrogen peroxide is formed by the action of bright sunlight or silent electric discharge on water and air. Chapman, Chadwick, and Ramsbottom (*J. Chem. Soc.* **91**, 947 (1907)) obtained a considerable yield of ozone by the action of ultra-violet rays on partially dried oxygen.

Davis (*U. S. Patent* 1209132, December 19, (1916)) has subjected air to violet and ultra-violet rays and partially ozonized it between a silica plate supported on an iron plate, and a glass disc having a layer of carbon. The iron and carbon plates are connected to terminals of an electric circuit, and air is drawn between the plates by a fan.

The various methods for the preparation of ozone and their probable mechanism have been discussed by Rideal and Kunz. (*J. Phys. Chem.* **24**, 379 (1920)).

Eucken (*Z. physik. Chem.* **107**, 436 (1923)) has investigated the formation of ozone by radiations of short wavelength, and observes a temperature coefficient less than unity. This behaviour is particularly noticeable at low oxygen pressures. Eucken attempts to explain this phenomenon by assuming that the mean life of activated molecules in high rotation states is shorter than when the rotational quantum number is less.

Very recently Vaughan and Noyes Jr. (*J. Amer. Chem. Soc.* **52**, 559 (1930)) have studied the photo-formation of ozone at atmospheric pressure in presence of radiations of wavelength below 1750 Å, which are not transmitted by quartz but are transmitted by fluorite. Oxygen has a region of continuous absorption below 1750 Å. The authors have observed that about two molecules of ozone are formed per quantum of radiation absorbed by oxygen in this region. It is suggested that in the region of continuous absorption, the temperature coefficient should be less than unity, unless the influence of the walls in removing the oxygen atoms is of importance.

Dadlez (*Compt. rend.* **185**, 89 (1927)) has determined the diminution of the ozone content of air at increasing distances from quartz lamps of various makes and candle powers. The symptoms produced in an adult after various periods in atmospheres containing different amounts of ozone have also been described.

Wendt, Landauer, and Ewing (*J. Amer. Chem. Soc.* **44**, 2377 (1922)) have noted that when chlorine is illuminated by a 2000 watt mercury lamp, no activation of the gas is noted, and no combination of this gas with hydrogen in the dark is observed. On the other hand, Venkataramaih (*J. Phys. Chem.* **27**, 74 (1923)) has stated that chlorine is activated by ultra-violet rays. The observation of Venkataramiah needs confirmation.

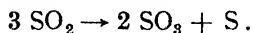
Radel (*Z. physik. Chem.* **95**, 378 (1920)) observed that when moist chlorine was illuminated, a fine cloud of single drops which grew rapidly in size was formed after an induction period which varied between one hundredth of a second and thirty seconds. On screening off the illumination, the particles decreased in size and finally disappeared. The same effect was observed when the chlorine was previously ionized. Irradiation of the reaction mixture with polonium, and with radium bromide produced the same effect, although this is considerably smaller than that produced by light.

Coehn and Tramm (*Ber.* **54**, 1148 (1921)) have shown that with a mixture of carbon monoxide and oxygen, whether it is dry or moist, on illumination with a quartz lamp, combination takes place to the extent of 4 to 5% within an hour. Thiele (*Z. angew. Chem.* **22**, 2472 (1909)) has reported that when carbon monoxide and oxygen are exposed to ultra-violet light, they combine less readily than hydrogen and oxygen under the same conditions. According to Humiston (*J. Phys. Chem.* **25**, 572 (1919)) carbon monoxide and fluorine do not combine when passed through a quartz tube illuminated with ultra-violet radiations.

Trautz (*Z. Elektrochem.* **21**, 329 (1915)) has investigated the formation of sulphuryl chloride SO_2Cl_2 from a mixture of sulphur dioxide and chlorine exposed to ultra-violet radiations in glass tubes heated to 291° . The reaction proceeds smoothly as a bimolecular one, especially at the high temperature. In addition to sulphuryl chloride, other products are also obtained. A temperature increase of 80° decreased the velocity of formation, and the reaction velocity has the temperature coefficient 0.88 for a 10° rise. Though the formation of sulphuryl bromide is not possible from sulphur dioxide and bromine on illumination, carbon oxybromide could be obtained from carbon monoxide and bromine on illumination.

On exposure to ultra-violet light, sulphuryl chloride decomposes into sulphur dioxide and chlorine. Le Blanc, Andrich, and Kangro (*Z. Elektrochem.* **25**, 229 (1919)) have investigated the reversible decomposition $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$ under radiations of different wavelengths. The light absorption by chlorine reaches a maximum at 3400 Å, and is almost nil at 2900 Å. On the other hand, the maximum absorption by sulphur dioxide takes place at this point with a minimum at 2400 Å. The absorption of light by sulphuryl chloride begins at 3000 Å, and rises rapidly for the shorter wavelengths. When radiations which are absorbed by sulphuryl chloride are used, the latter decomposes completely at 55° and 100° . With mixtures of sulphur dioxide and chlorine the radiations absorbed by the former cause only slight changes which are probably side reactions, and not the formation of sulphur oxychloride; while radiations which are absorbed by chlorine only cause the reaction to run to an equilibrium, the position of which depends on the temperature and the amount of water vapour.

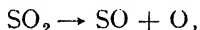
Hill (*Trans. Faraday Soc.* **20**, 107 (1924)) has reported that the decomposition of gaseous sulphur dioxide in ultra-violet rays from an uviolet mercury vapour lamp takes place according to the equation:



By using different filters it was observed that radiations of wavelength 3130 Å lying within the absorption band of sulphur dioxide are most active. Shorter wavelengths are ineffective because of their low intensity.

Very recently Henri (*Nature* **125**, 275 (1930)) has shown that the absorption spectrum of SO₂ vapour is composed of three electronic regions: the first 3900—3400 Å, which appears at high pressure in a tube at $p = 100$ cms., the second 3370—2450 Å, which begins to appear at $p = 0.1$ mm., and the third from 2350—2000 Å for very low pressures.

The first and third regions are made up of series of bands with a fine rotation structure. The second region is also made up of bands with fine structure, but between 2550 Å and 2500 Å, the bands become broad and diffuse. The molecule is then pre-dissociated. If we assume that this pre-dissociation limit corresponds to the reaction:



the heat of this reaction must be between 111,000 (2550 Å) and 114,000 (2500 Å) calories, the mean value being 112,500 cal.

Coehn and Becker (*Z. physik. Chem.* **70**, 88 (1910)) have investigated the formation of sulphur trioxide from sulphur dioxide and oxygen, when irradiated by ultra-violet light. With a mixture of one part of sulphur dioxide with one of oxygen, equilibrium is attained with the production of 65% sulphur trioxide. This equilibrium can also be attained starting from sulphur trioxide. At 160°, with the gases confined in the reaction chamber, equilibrium was reached in one hour. Coehn and Becker consider that an industrial photochemical process for the production of sulphuric acid is feasible, since on using air in place of oxygen no oxides of nitrogen are formed.

Dhar (*J. Phys. Chem.* **28**, 948 (1924)) has obtained crystals of sulphur trioxide by exposing a mixture of sulphur dioxide and oxygen at the ordinary temperature to tropical sunlight.

Norrish and Rideal (*J. Chem. Soc.* **125**, 2070 (1924)) have shown that the reaction between hydrogen and sulphur is accelerated by ultra-violet rays from a mercury vapour lamp. The absorption spectrum of sulphur vapour contains a band with maximum absorption at 2750 Å, and radiations of wavelength 2700 Å are active in initiating a gaseous reaction between hydrogen and sulphur vapour, the velocity of the reaction being proportional to the pressure of the sulphur vapour. Norrish and Rideal assume that in the gaseous state, reactions between hydrogen and sulphur take place only with sulphur atoms, which are produced by photochemical dissociation and collisions.

Recently Warburg (with Rump) (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, **29**, 624 (1929)) has studied the photolysis of solutions of hydrogen sulphide in hexane and water. Hydrogen sulphide decomposes in light into sulphur and hydrogen. In hexane, the quantum yield is unity, in water the yield is 0.2 to 0.3. According to Warburg, photolytes may be divided into two groups according to whether reaction between the photolyte and the solvent occurs or not. Hydrogen sulphide in water belongs to the former class, but in hexane solution it belongs to the second class.

Curtis (*J. Amer. Chem. Soc.* **42**, 720 (1920)) reports that solutions of aniline green and magenta are not bleached when exposed to a quartz mercury lamp, neither they are decolorized by the addition of 3% hydrogen peroxide to them, unless the mixture is illuminated. Holmes (*J. Amer. Chem. Soc.* **44**, 1002 (1922)) has stated that solutions of magenta, malachite green, methyl violet, and crystal violet, which have been decolorized by sulphur dioxide, when exposed to ultra-violet light develop their original colours.

When illuminated by a large mercury vapour lamp, ammonia is decomposed almost completely in two hours; with hydrogen phosphide the decomposition is evident in a few minutes. Hydrogen arsenide, zinc ethyl, and carbonyl chloride are readily decomposed, while sulphur fluoride and methane are hardly decomposed.

According to Stock and Friederici (*Ber.* **46**, 1959 (1913)), the slow decomposition of boron hydride B_4H_{10} to the hydride B_2H_6 is accelerated markedly by illumination by ultra-violet rays. At 100° the photo-decomposition is complete in a few hours.

Marmier (*Compt. rend.* **154**, 32 (1912)) has shown that solutions of sodium thiosulphate decompose in ultra-violet light.

Plotnikoff (*Chem. Ztg.* **52**, 669 (1921)) has shown that neither ammonium, potassium, nor sodium chromate suffers any change when exposed to the most intense sunlight. In presence of inorganic or organic reducing agents, however, photochemical changes take place (compare Dhar, *J. Chem. Soc.* **111**, 707 (1917)). Plotnikoff has studied qualitatively the photo-oxidation of numerous organic compounds by dichromates.

Ross (*J. Amer. Chem. Soc.* **28**, 788 (1906)) has observed that when a solution of potassium iodide is exposed in an open vessel to the ultra-violet radiations from a spark, iodine is liberated, and a portion of the iodine set free is due to the presence of ozone and oxides of nitrogen formed by the passage of the spark through air. According to Kailan (*Monatsh.* **33**, 71, 1329 (1912)) strontium iodide in neutral

aqueous solutions decomposes most rapidly, while barium iodide seems to decompose faster than potassium and magnesium iodides.

Suryanarayana (*J. Science. Assoc. Maharajah's College, Vizianagram* **2**, 12 (1924)) has investigated the stability of aqueous solutions of potassium iodide, nitrate, and chlorate in ultra-violet light. Dhar and Sanyal (*J. Phys. Chem.* **29**, 926 (1925)) have shown that in tropical sunlight solutions of potassium nitrate decompose rapidly, whilst solutions of potassium chlorate are converted into chloride and oxygen on long exposure.

Very recently Meiler and Noyes Jr. (*J. Amer. Chem. Soc.* **52**, 527 (1930)) have shown that oxygen is evolved from solid potassium chlorate when exposed to radiations of wavelengths shorter than 2800 Å. These authors have also observed the decomposition of potassium chlorate by slow speed electrons having kinetic energy corresponding to 22 volts.

Mathews and Curtis (*J. Phys. Chem.* **18**, 641 (1914)) have shown that solutions of potassium iodate decompose, liberating iodine, when exposed to ultra-violet light at 30°. The photolysis is accelerated by carbon dioxide, and retarded by oxygen, so much so that iodine is not liberated when the solution is kept saturated with oxygen in an atmosphere of oxygen. Dhar and Sanyal (loc. cit.) have shown that iodine is set free when crystals of iodic acid are exposed to sunlight. Oertel (*Biochem. Zeit.* **60**, 480 (1914)) has shown that by the action of ultra-violet light, aqueous solutions of chlorates, bromates, iodates, and periodates are decomposed into oxygen and the halides, and the reaction appears to be quantitative with a sufficiently long period of illumination. In the case of perchlorates, there was only slight decomposition. The velocity of the photo-decomposition is in the order: Bromate > iodate > chlorate.

Ross (*J. Amer. Chem. Soc.* **28**, 790 (1906)) has studied the decomposing action of ultra-violet light on ferric salts, and has shown that the conversion of ferric salts to the ferrous state is greatly accelerated by organic substances. Similar observations have been made by Benrath (*Z. physik. Chem.* **74**, 115 (1910)).

According to Urbain and Scal (*Compt. rend.* **168**, 887 (1919)), tetrachlorides of titanium, tin, and carbon are decomposed with the liberation of chlorine, when illuminated by arc light. Pougnet (*Compt. rend.* **161**, 348 (1915)) has reported that on exposing a solution of mercuric chloride to ultra-violet light from a mercury vapour lamp, it becomes turbid due to the formation of calomel. The decomposition is increased with the time of exposure, but the reaction is re-

versible. Skinner (*Proc. Cam. Phil. Soc.* **12**, 260 (1904)) has observed that mercurous sulphate darkens rapidly on exposure to light. Sanyal and Dhar (*Z. anorg. Chem.* **123**, 212 (1923)) have investigated the photochemical decomposition of several solid salts of lead, bismuth, mercury, copper, and silver in sunlight. Lead bromide is the most sensitive among the lead salts, and on exposure to sunlight for 75 hours, 8–10 % of the bromide decomposes with liberation of bromine. Amongst the bismuth salts the oxychloride decomposes most quickly. After 75 hours' exposure 0.8–1 % is decomposed. In the case of the lead salts, the light sensitiveness is increased to a greater extent in presence of an excess of bromide than in presence of an excess of lead nitrate or acetate. The light sensitiveness depends a good deal on the method of preparation of the solid substances.

Gortner (*Amer. Chem. J.* **39**, 157 (1908)) investigated the colour change of different kinds of glass in sunlight, and reported that glass which is relatively rich in manganese (0.2 to 0.3 per cent) becomes violet coloured in less than a month, and the degree of coloration is proportional to the manganese content. The violet colour is readily destroyed by heating the glass.

Roches (*Rev. Chim. Ind.* **31**, 109 (1922)) believes that the blackening of lithopone under the action of sunlight or ultra-violet rays is due to the presence of impurities, and specially of chlorine. Maas and Kempf (*Z. angew. Chem.* **36**, 293 (1923)), however, report that the blackening of lithopone on exposure to light is due to the calcined zinc sulphide it contains. They are of opinion that the phenomenon is caused by the formation of zinc disulphide and metallic zinc on exposure to light, and that the mechanism of the process is probably the same as that assumed by Fajans (*Z. physik. Chem.* **97**, 478 (1921)) regarding the action of light on silver bromide.

Job and Emschwiller (*Compt. rend.* **177**, 313 (1923)) have studied the problem of the darkening of certain zinc pigments, and have concluded that all varieties of white zinc sulphide which blacken under the influence of light must have been heated, must contain some impurities, and must not be completely anhydrous. The grey colour of the exposed sulphide is very likely due to the presence of zinc. When zinc sulphide is suspended in water in a quartz vessel and illuminated by mercury arc light, zinc and sulphur are formed. Hydrogen is also liberated in the process, due partly to the action of zinc on water, and partly to the formation of hydrogen sulphide, which is also decomposed. Some zinc salt of a thionic acid is also formed in the process. Schleede, Herter, and Koratzki (*Z. physik. Chem.* **106**, 386 (1923)) have

also noticed that no blackening is shown by precipitated zinc sulphide unless it has been first ignited. The presence of halogens, especially in combination with heavy metals, increases the light sensitiveness of the ignited material.

Pfund (*Proc. Amer. Soc. Testing Materials* **23**, II, 375 (1923)) has shown that wavelengths greater than 3200 Å show very little darkening influence on light sensitive lithopone. In recent years marked improvements have been effected in the stability of lithopones towards light.

Wassiljewa (*Z. wiss. Photochem.* **12**, 1 (1913)) has shown that colloidal tungstic acid, formed from sodium tungstate and a slight excess of hydrochloric acid, is reduced to an intense blue solution when exposed to light with reducing agents, e.g. formaldehyde, sucrose, dextrose etc. If the colloid is allowed to "age", it has been observed that the above reduction process does not take place when exposed to light. On raising the temperature, however, the blue reduction products are formed, as in the case of the freshly prepared colloidal solution.

Recently, Ghosh and Mukerji (*J. Indian Chem. Soc.* **6**, 321 (1929)) have shown that the velocity of the oxidation of dextrose by hydrogen peroxide in presence of colloidal tungstic acid and an excess of hydrochloric acid is almost negligible in the dark, but is accelerated by ultra-violet radiations (3300—4000 Å). Oxidation of 1 mol of dextrose corresponds with the decomposition of 1 mol of hydrogen peroxide.

Schwarz and Tiede (*Ber.* **60**, B, 69 (1927)) have stated that in light, solutions of potassium ferricyanide decompose after intense illumination into ferric hydroxide, cyanogen, and potassium ferrocyanide. With potassium cobalticyanide, the change is $K_3Co(CN)_6 + H_2O = K_3Co(CN)_5OH + HCN$ and $K_3Co(CN)_6 + H_2O = KCN + K_2Co(CN)_5H_2O$. The corresponding chromium compound behaves similarly to the cobalticyanide, whereas the manganese compound rapidly decomposes into manganic hydroxide, hydrocyanic acid, and potassium cyanide even in absence of light.

According to Plotnikoff and Karschulin (*Z. Elektrochem.* **33**, 212 (1927)) the absorption bands of potassium ferricyanide and of green and brown ferric ammonium citrate extend to the infra-red, but the region of photochemical sensitiveness does not extend into the infra-red. The use of gelatine coated on glass instead of sized paper, as the medium for the light sensitive substances, results in a shift of the sensitivity maximum towards the longer wavelengths, and an alteration in the general sensitivity.

Dhar (*J. Chem. Soc.* **111**, 694 (1917); *Z. anorg. Chem.* **128**, 212 (1923)) observed that a solution of potassium cupri-oxalate is decom-

posed in light, and that the velocity of this photochemical reaction is greatly accelerated by ferric and uranyl salts. Recently, Bhagwat, Dube, and Dhar have started quantitative investigation of this reaction. In presence of ferric chloride, the velocity of the photochemical decomposition of potassium cupri-oxalate appears to be zero-molecular in sunlight, and is independent of the concentration of the photolyte. A large excess of potassium oxalate retards the reaction. Similar results have been obtained by Allmand and Webb (*J. Chem. Soc.* 1518 (1929)) in the photolysis of potassium ferri-oxalate. Carbon dioxide and oxygen also inhibit the photolysis of potassium cupri-oxalate. The relation between the concentration of the sensitizer and the velocity of the reaction exhibits a maximum, and very high concentrations of the sensitizers actually retard the reaction. The temperature coefficient of the reaction for a 10° rise is 1.13. There is practically no decomposition in the artificial light from a 1000 Watt gas-filled tungsten filament lamp. It therefore appears probable that only ultra-violet rays are active in the photolysis of potassium cupri-oxalate. The quantum yield is less than unity in sunlight.

Gleu (*Ber.* 61 B, 702 (1928)) has shown that solutions of azoimide acidified with sulphuric acid, when exposed to ultra-violet light, decompose with evolution of almost pure nitrogen and formation of hydroxylamine, accompanied by a very small proportion of ammonia. The course of the photochemical change is independent of the concentration of sulphuric acid. It is suggested that the reactions involved are:



Increase in the concentration of hydrochloric acid favours the production of ammonia to a remarkable extent, and the change induced in the ratio N: H suggests the simultaneous formation of nitrous oxide. The reaction is thus represented: $\text{HN}_3 = \text{NH} + \text{N}_2$; $\text{NH} + \text{HCl} = \text{NH}_2\text{Cl}$; $\text{NH}_2\text{Cl} + 2 \text{HCl} = \text{NH}_4\text{Cl} + \text{Cl}_2$. Production of nitrous oxide is ascribed to slow oxidation of hydroxylamine by chlorine. Neutral or alkaline azoimide when exposed to light forms hydrazine, along with ammonia and hydroxylamine, and the evolved gases contain nitrogen and hydrogen.

Beckman and Dickinson (*J. Amer. Chem. Soc.* 50, 1870 (1928)) have reported that brief illumination by ultra-violet radiation causes 27% of the azoimide to decompose into nitrogen and hydrogen, and the remainder into nitrogen and ammonia.

Beckman and Dickinson (*J. Amer. Chem. Soc.* 52, 124 (1930)) have

recently determined the quantum yield in the photo-decomposition of azoimide (HN_3) in monochromatic radiation of wavelength 1990 Å over a pressure range varying from 2 to 130 mm. The quantum yield over this pressure range is 3.0 ± 0.5 molecules of HN_3 decomposed per quantum absorbed.

In the total radiation from an aluminium spark the velocity of decomposition of HN_3 at pressures varying from 0.06 to 0.5 mm. has been found to be proportional to the pressure, and this indicates constancy of quantum yields also over this pressure range.

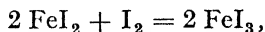
The authors state that in spite of the high concentration of energy involved in the primary process, and the highly explosive nature of HN_3 , there is no tendency towards chain reaction even at a pressure of 130 mm.

This reaction appears to be similar to the photo-decomposition of gaseous azomethane investigated by Ramsperger (*J. Amer. Chem. Soc.* **50**, 123 (1928)). In the photo-decomposition of azomethane, which has also an explosive character, low quantum yields were obtained by Ramsperger.

Doran and Gillam (*J. Soc. Chem. Ind.* **47**, 259 (1928)) have obtained a polymeride of carbon monosulphide, as a reddish brown solid, by irradiation of mixtures of carbon disulphide and carbon tetrachloride by means of a vita-glass screened mercury vapour lamp.

Bhatnagar, Anand, and Gupta (*J. Indian Chem. Soc.* **5**, 49 (1928)) have investigated the influence of polarized and heterogenous light of equal intensities on the reaction between ammonium oxalate and mercuric chloride, and the decomposition of alkaline hydrogen peroxide. From their previous results (*Nature* **117**, 302, **118**, 11 (1926)) it is concluded that polarized light possesses a selective effect only in heterogeneous systems. Anand and Bhatnagar (*Z. physikal. Chem.* **131**, 134 (1928)) have studied the influence of polarized rays on the reaction between sodium and potassium amalgams and water. They have supported the view that the first stage in a photochemical reaction consists in the liberation of electrons.

Padoa and Miss Vita (*Gazzetta* **58**, 461 (1928)) have carried on comparative experiments on the yields of the reaction:



when illuminated by continuous and intermittent light respectively. In general the yield was increased by the use of intermittent light, but the augmentation depended both on the wavelength of the light, and on the frequency of interruption of the illumination.

W. A. Noyes Jr. (*J. Amer. Chem. Soc.* **49**, 3100 (1927); **50**, 49 (1928); *Z. physikal. Chem. B.* **2**, 445 (1929)) has shown that the photochemical reaction between oxygen and mercury vapour at low pressures occurs largely between ozone and mercury vapour. It is suggested that a relatively unstable complex of excited mercury and oxygen is formed, which yields ozone through collision with activated or unactivated oxygen molecules, or with ozone molecules.

Leipunsky and Sagulin (*Z. physik. Chem. B.* **1**, 362 (1928)) have also investigated the oxidation of mercury vapour under the influence of light from the mercury arc, and also by bombardment with electrons emitted by glowing platinum and accelerated by different voltages. Only the line 2537 Å appears to be photochemically active. The velocity of the reaction is not affected by electrons accelerated by a field of less than five volts, which is the value of the first resonance potential of mercury. It is assumed that a chain reaction takes place. The results show that contrary to the observations of Noyes (*loc. cit.*), the reaction is due to excited mercury atoms only, and the primary formation of ozone has not much influence.

Bhatnagar, Yajnik, and Zadoo (*J. Indian Chem. Soc.* **4**, 209 (1927)) have investigated the interaction of the following pairs of sols in presence of light and air:

- (1) silver sol and arsenious sulphide sol,
- (2) silver sol and antimony sulphide sol,
- (3) gold and arsenious sulphide sols and
- (4) gold and antimony sulphide sols.

These interactions are assumed to be photochemical in nature, and chemical analysis of the mixtures when they had attained the final colour revealed the formation of the sulphide of the metal, free sulphur, and antimonious or arsenious acid.

Recently Mooney and Ludlam (*Trans. Faraday Soc.* **25**, 442 (1929)) have shown that ethylene when illuminated by radiations of wavelengths shorter than 2110 Å is decomposed, forming acetylene as one of the products of the decomposition. Radiations of wavelengths shorter than 1990 Å are completely, and 2020 Å about 75% absorbed by ethylene.

CHAPTER XVIII.

The Action of Light on diverse Organic Compounds.

The action of light on organic compounds depends a great deal upon the wavelength of the radiation used. Broadly speaking the shorter the wavelength the more drastic is the decomposition of the organic molecule, and it can be stated roughly that no fundamental or deep-seated change in the organic molecule can be expected with radiations of wavelengths greater than 2500 Å in absence of air. Not only decompositions of organic substances, but oxidation, reduction, polymerization, and synthesis are facilitated by light. The late Professor Daniel Berthelot was a pioneer in this direction.

In the following tables and the explanatory notes, the general position regarding the photochemistry of organic compounds is indicated and summarized:

PHOTOCHEMICAL DECOMPOSITIONS.

Substance	Products		Reference
Acetic acid (in absence of air) in ultra-violet rays	Hydrogen	13%	Berthelot and Gaudechon (<i>Compt. rend.</i> 156 , 233 (1913); <i>Travaux scientifiques de Daniel Berthelot, Paris</i> (1917), pp. 116—140)
	Carbon dioxide . .	41%	
	Carbon monoxide	14%	
	Methane	13%	
	Ethane	19%	
Propionic acid	Hydrogen	15%	,,
	Carbon dioxide	41%	
	Carbon monoxide	15%	
	Methane	15%	
	Butane	14%	
Acetaldehyde	Hydrogen	33%	,,
	Carbon dioxide	5%	
	Carbon monoxide	39%	
	Ethane	23%	

Substance	Products	Reference
Propaldehyde	Hydrogen 37% Carbon dioxide 6% Carbon monoxide 37% Butane 20%	Berthelot and Gaudechon (<i>Compt. rend.</i> 156 , 233 (1913); <i>Travaux scientifiques de Daniel Berthelot, Paris</i> (1917) pp. 116—140)
Ethyl alcohol	Hydrogen 63% Carbon monoxide 22% Ethane 15%	„
Propyl alcohol	Hydrogen 69% Carbon monoxide 16% Butane 15%	„
Acetone in ultra-violet light	Carbon monoxide 49% Ethane 46% Methane 5%	„
Acetone in sunlight	Methane and acetic acid	„
Acetone in aqueous solution in monochromatic light	Acids	Henri and Wurmser (<i>Compt. rend.</i> 155 , 503 (1912))
Glycerol (10% aqueous solution) in ultra-violet light	Formaldehyde, acids etc. (H_2O_2 facilitates this decomposition)	Henri and Ranc (<i>Compt. rend.</i> 154 , 1261 (1912))
Glycerol-water system (Alkaline)	Glycerose, glyceric aldehyde β -acrose	Bierry, Henri, and Ranc (<i>Compt. rend.</i> 152 , 535 (1911))
Aqueous glycerol (in presence of air and sunlight)	Reducing sugars and formaldehyde	Dhar and Sanyal (<i>J. Phys. Chem.</i> 29 , 926 (1925))
Lactic acid	Acetic acid but no methane or alcohol	Baudisch (<i>Biochem. Z.</i> 103 , 59 (1920)); Mangold and Williams (<i>Z. angew. Chem.</i> 36 , 456 (1923))
Calcium lactate (solid)	Carbon monoxide, hydrogen, methane, and ethane	Berthelot and Gaudechon (<i>Compt. rend.</i> 151 , 478 (1910))

Substance	Products	Reference
Oxalic acid	Carbon dioxide and formic acids $\text{HCOOH} = \text{CO} + \text{H}_2\text{O}$ glyoxalic acid, carbon monoxide, carbon dioxide, water	} Discussed previously Baur (<i>Z. physik. Chem.</i> 111 , 315 (1924))
Urea, amines, amides, hydroxylamine, guanidine, acetonitriles, etc. in ultra-violet rays in presence of air	Ammonia and ammonium nitrite	Berthelot and Gaudechon (<i>Compt. rend.</i> 152 , 522 (1911))
Formamide in ultra-violet rays	Hydrocyanic acid	Ibid. 150 , 1164 (1910))
Ethyl Acetoacetate, Acetylacetone	Ethyl acetate, acetone, acetic acid etc.	Grossmann (<i>Z. physik. Chem.</i> 109 , 305 (1924))
Benzil in the vapour state	Benzophenone and carbon monoxide	} Porter, Ramsperger and Steel (<i>J. Amer. Chem. Soc.</i> 45 , 1827 (1923))
Benzil in dilute alcoholic solution	Benzoic acid, benzaldehyde, and benzoin	
Diacetyl vapour in presence of water vapour	Ethane, carbon monoxide, acetaldehyde, acetic acid	
Carbon disulphide in ultra-violet light; carbon disulphide in sunlight	Sulphur is set free and there is a tendency to form yellow resinous substances. On exposure for a short time it becomes orange red; on longer exposure, black deposit of carbon is obtained.	Bruhat and Pauthenier (<i>Compt. rend.</i> 178 , 1536 (1924)) Dhar and Sanyal (<i>J. Phys. Chem.</i> 29 , 926 (1925))
Cis- and trans- α - β di-iodoethylene, α - α di-iodoethylene	Decomposition with liberation of iodine	Kaufmann (<i>Ber.</i> 55 , 249 (1922))
Alkyl halides	Halogens liberated.	Stobbe and Schmitt (<i>Z. wiss. Phot.</i> 20 , 57 (1920)); Burke and Connan (<i>J. Chem. Soc.</i> 85 , 574 (1904)); Iredale (<i>J. Phys. Chem.</i> 3 , 290 (1929)); Jobard-Emschwiller (<i>Compt. rend.</i> 179 , 52 (1924))

Substance	Products	Reference
Toluene	Slight decomposition with formation of benzaldehyde, benzoic, and formic acids. Hydrocarbons and condensation products of benzaldehyde	Kailan (<i>Monatsh.</i> 40 , 445 (1920))
Ethane in mercury lamp	Methane and hydrogen, and a product of unknown composition	Tolloczko (<i>Chem. Zentr.</i> II , 546 (1927))
Starch in aqueous solution	Hydrolysis and partial oxidation with formation of dextrans, maltose, pentose, reducing sugars, formaldehyde etc.	Massol (<i>Compt. rend.</i> 152 , 902 (1911)); Bielecki and Wurmser (<i>ibid.</i> 154 , 1429 (1912))
Cellulose in radiations from mercury vapour lamp in air	Oxycellulose, and tensile strength lost	Dorée and Dyer (<i>J. Soc. Dyers and Col.</i> 33 , 17 (1917))
Tartaric acid in one percent solution after 3 hours' exposure to ultra-violet rays	3.5 c. c. of gaseous mixture containing CO ₂ = 66% CO = 10% H ₂ = 21% Hydrocarbon = 3%	Volmar (<i>Compt. rend.</i> 176 , 742 (1923))
Saturated liquid hydrocarbons and pinene exposed to ultra-violet rays	Acetylene, ethylene, and hydrogen, with liberation of carbon	Urbain and Scal (<i>Compt. rend.</i> 168 , 887 (1919))
Solid lead phthalate exposed to ultra-violet rays	Yellowish brown substance, probably lead oxide	Ekely and Banta (<i>J. Amer. Chem. Soc.</i> 39 , 762 (1917))
Celluloid exposed to ultra-violet light	Becomes brown and brittle with liberation of gaseous products	Holmes and Patrick (<i>J. Phys. Chem.</i> 26 , 25 (1922))
Explosives cut into cylinders weighing 0.24 to 0.45 gm. Powders, cordite, nitroglycerine, etc. when exposed to ultra-violet rays	Rapidly decomposed to gaseous products	Berthelot and Gaudechon (<i>Compt. rend.</i> 153 , 1220 (1911); 154 , 201, 514 (1912))

Substance	Products	Reference
Diazo camphor in benzene solution in ultra-violet rays	Undergoes decomposition	Mangold and Williams (<i>Z. angew. Chem.</i> 36 , 456 (1923))
Thymine in air when exposed to ultra-violet rays (catalyzed by ferrous sulphate).	Urea and pyruvic acid	Bass (<i>J. Amer. Chem. Soc.</i> 46 , 190 (1924))
Malachite green in sunlight	Formaldehyde in small amount and amines, in alkaline conditions nitrites	Burk (<i>J. Amer. Chem. Soc.</i> 49 , 1818 (1927))

SUGARS.

According to Berthelot (*Travaux scientifiques, Paris 1917*, pp. 135 to 136) an aqueous solution of glucose begins to decompose under the influence of radiations of wavelengths 3000 Å—2500 Å into gaseous products containing 2 volumes of carbon monoxide and one volume of hydrogen, but in presence of radiations of wavelengths shorter than 2500 Å, carbon dioxide and methane are produced, and the proportion of hydrogen formed increases. All the aldehydic sugars decompose in radiations 3000 Å—2500 Å in the following way:

	Carbon monoxide	Hydrogen
Glucose	2 vols.	1 vol.
Galactose	"	"
Mannose	"	"
Maltose	"	"
Lactose	"	"

The ketonic sugars begin to decompose in sunlight and in ultra-violet radiations. Dioxycetone, erythrulose, laevulose, sorbose, etc. decompose with the liberation of pure carbon monoxide. Although laevulose or sorbose contains five alcoholic groups and one ketonic group, only the ketonic link is the first to be attacked in presence of light.

Finally, the purely alcoholic sugars or polyols are more resistant to light, and they are not decomposed by radiations of wavelengths 3000—2500 Å. These decompose in radiations 2000 Å, however, and give out equal volumes of carbon monoxide and hydrogen.

	Carbon monoxide	Hydrogen
Erythritol	1 volume.	1 volume.
Mannitol	"	"

According to Abelous, Aloy, and Valdiquié (*Compt. rend. Soc. Biol.* **96**, 1385 (1927)) laevulose, and other sugars obtained by hydrolysis of carbohydrates, readily decompose in sunlight with formation of aldehydic substances, particularly formaldehyde.

The photochemical decomposition of sucrose can be followed by measurements of optical rotation, acidity, reducing power, and collecting the gaseous products formed. Euler and Ohlsen (*J. Chim. phys.* **9**, 616 (1911)) observed that hydrolysis of cane sugar took place in radiations of the mercury vapour lamp, and small amounts of acids were also formed. Dhar and collaborators (*Z. anorg. Chem.* **119**, 177 (1921)); **134**, 172 (1924)); *J. Indian Chem. Soc.* **6**, 879 (1929)) have shown that cane sugar inversion is accelerated by sunlight and radiations of wavelengths 4725, 5650, and 7304 Å. The quantum yield and temperature coefficients have been measured.

Andant and Rousseau (*Compt. rend.* **186**, 365 (1928)) have studied the formation of dextrose from sucrose containing 1% sulphuric acid and magnesium sulphate in the light of the mercury vapour lamp. The photolytic effect of the infra-red radiations was of the same order as that of the total naked arc, whilst that of radiation 3650 Å appeared to be greater. The authors conclude that this is an example of the antagonistic effect of rays of different wavelengths. These results seem very peculiar and need confirmation. Bierry, Henri and Ranc (*Compt. rend.* **152**, 1629 (1911)) observed the formation of formaldehyde, carbon monoxide, carbon dioxide, and hydrogen, after 2 or 3 days exposure of sugar solution to ultra-violet light. Beyersdorfer and Hess (*Ber.* **57 B**, 1708 (1924)) have observed that cane sugar on illumination is first inverted, and then that organic acids, ketones, alcohols, aldehydes, carbon monoxide, carbon dioxide, hydrogen, and methane are produced. Condensation products, such as dextrin and caramel, are also formed. These authors have also examined the effect of adding green colouring matters, such as chlorophyll and Badische green PLX, to aqueous solutions of sucrose, but no decomposition was observed in visible light.

Berthelot and Gaudechon (*Compt. rend.* **155**, 1153 (1912)) have claimed that the decomposition of laevulose can be used as an ultra-violet actinometer, the volume of gas mixture liberated by a 10% aqueous solution being proportional to the time of exposure; but Bierry and Ranc (*Bull. Soc. Chim.* **35**, 771 (1924)) have stated that the photochemical decomposition of laevulose is much more complicated than is assumed by Berthelot and Gaudechon, and that carbon dioxide and formaldehyde are also formed along with carbon monoxide.

ORGANIC IODIDES.

According to Stobbe and Schmidt (*Z. Phot.* **20**, 57 (1920)), oxygen is necessary for the photochemical decomposition of solutions of the alkyl iodides.

Job and Emschwiller (*Compt. rend.* **179**, 52 (1924)) have stated that oxygen is not necessary, and that in complete absence of oxygen ethyl iodide is decomposed in light with the liberation of iodine, ethylene, and ethane, and small amounts of butane and hydrogen. Similar results are obtained with methyl iodide. When a tube containing ethyl iodide is placed in the spectrum of the carbon arc, the decomposition begins in radiations of wavelength 4100 Å, and goes on increasing as the light frequency increases. Recently, Iredale (*J. Phys. Chem.* **33**, 290 (1929)) has determined the quantum efficiency of the photo-decomposition of ethyl iodide in radiations of wavelengths 3650 and 3100 Å. Alcoholic solution of ethyl iodide has an absorption band at 2600 Å, and it also absorbs at 3650 Å when a column of the liquid several centimetres long is used. To isolate the region 3650 Å, a Winther filter (*Z. Elektrochem.* **19**, 389 (1913)) of neutral diamond fuchsin (0.03% solution in 1 cm. thickness) was used. Transmission of the lines 3130 and 3340 Å is negligible, and the small amounts of radiations 4040 Å and red lines were not appreciably absorbed by ethyl iodide. Iredale's experimental results show that the quantum yield is nearly unity, and that the photochemical decomposition of liquid ethyl iodide appears to be a very simple process, one quantum effecting the detachment of an iodine atom from a molecule of ethyl iodide.

ACETALDEHYDE.

The investigations of Berthelot and Gaudechon (*Compt. rend.* **156**, 233 (1913)) with acetaldehyde show that, in the absence of oxygen, ultra-violet light of long wavelength does not convert aldehyde into acetic acid. In presence of medium and extreme ultra-violet rays, oxidation takes place even in absence of oxygen, and a portion of the acetaldehyde is converted into acetic acid, the amount of acid formed being greater in the form of vapour than in the liquid condition. With rays of wavelength 2500 Å, polymerization is rapid, both para- and met-aldehyde being formed. The presence of water checks polymerization, but favours acidification, and formic acid is formed. Of the three compounds (e. g. acetaldehyde, ethyl alcohol, and acetic acid) studied by Berthelot and Gaudechon (*Compt. rend.* **156**, 68 (1913)) for comparative results, only acetaldehyde is decomposed by sunlight. Rays from a mercury

lamp, screened by thin glass, which absorbs radiations shorter than 3000 Å, decompose acetaldehyde in accordance with the equation $\text{CH}_3\text{CHO} = \text{CO} + \text{CH}_4$. Direct rays from a mercury vapour lamp photolyse not only acetaldehyde but ethyl alcohol and acetic acid. Ethyl alcohol is decomposed primarily into acetaldehyde and hydrogen, but usually some carbon monoxide and ethane are also formed.

ORGANIC ACIDS.

Ultra-violet light causes the decomposition of organic acids and their salts, but with unsaturated compounds polymerization and isomerization characteristic of multiple bonds take place.

Kailan (*Monatsh. Chem.* **34**, 1209 (1913)) has found that when 0.5 to 2 N solutions of acetic, oxalic, malonic, succinic, malic, and tartaric acids are exposed to ultra-violet light from a quartz lamp, slight decomposition takes place. The decomposition velocity increases with the introduction of an alcoholic hydroxyl group in the molecule. Volmar (*Compt. rend.* **176**, 742 (1923)) has reported that one per cent tartaric acid solution on exposure to ultra-violet light gives out CO_2 , CO, H_2 , and hydrocarbons, and that the solution contains aldehydes and small quantities of reducing sugars. Similar observations were made by Euler and Ryd (*Biochem. Z.* **51**, 97 (1913)). Ferric and uranyl salts accelerate this decomposition. Benrath and Obladen (*Z. wiss. Phot.* **22**, 65 (1929)) have studied the photo-reduction of titanate salts by mandelic and lactic acids.

Volmar (*Compt. rend.* **176**, 1465 (1923)) has observed that solutions of potassium antimony tartrate, and the corresponding compounds of arsenic, bismuth, copper, and iron decompose in ultra-violet light with liberation of the metal, the maximum effect being obtained with the bismuth compound.

The photochemical decomposition of Fehling's solution has been investigated by different workers. Byk (*Z. physik. Chem.* **49**, 659, 679 (1904)) has observed that radiations shorter than 4000 Å can decompose Fehling's solution. Bolin and Linder (*Z. physik. Chem.* **93**, 721 (1919)) have shown that in quartz vessels the temperature coefficient between 15° and 25° has the value 1.2. The velocity of the reaction increases with the time of illumination, and when the light is removed the reaction continues for some time. The light source used by Bolin and Linder was the carbon arc.

According to Euler and Ryd (*Biochem. Z.* **51**, 97 (1913)) the photochemical decomposition of lactic acid by short ultra-violet rays is

analogous to fermentation, with evolution of carbon dioxide. Holmes and Patrick (*J. Phys. Chem.* **26**, 25 (1922)) have observed that when silica gels impregnated with acetic acid or acetone are irradiated with ultra-violet radiations, they give off gaseous products.

Cassel (*Z. physik. Chem.* **92**, 113 (1916)) has shown that under the influence of ultra-violet light of wavelength 2500 Å, bromoacetic acid and alcohol and chloroacetic acid and alcohol react to form methyl alcohol, acetaldehyde and the halogen acids. Euler (*Ber.* **49**, 1366 (1916)) has reported that the velocity of the decomposition of halogen acetic acids in dilute aqueous solutions at 18° when exposed to ultra-violet radiations is practically the same as that of the dark reaction at 100°. The photo reaction appears to be of a lower order than the dark reaction.

Piutti (*Chem. Zentr.* **I**, 2514 (1924)) has observed that chloropicrin acts as an oxidizing, chlorinating, or nitrating agent respectively, according to the compound with which it is exposed to light. According to Custis (*J. Franklin Inst.* **184**, 876 (1917)), trinitro-toluene darkens in colour on strong illumination. Bass and Johnson (*J. Amer. Chem. Soc.* **46**, 456 (1924)) have investigated the effect of ultra-violet light on the oxidation of toluene by nitrogen peroxide. Custis (*J. Franklin Institute* **184**, 878 (1917)) has studied the influence of ultra-violet light on nicotine and pyridine. According to Rossi (*Chem. Zentr.* **82**, II (1911)) the oxidation of phenolphthalein by hydrogen peroxide is accelerated by light. Baudisch and Furst (*Ber.* **45**, 3426 (1912)) have observed that the ammonium salt of α -nitrosonaphthyl hydroxylamine undergoes decomposition in light. Piutti (*Atti R. Acad. Lincei.* (V), **22**, II (1913)) has noted that in the transformation of santonin into photosantonin acid and isosantonin acid in light, there are intermediate steps.

Morgan, Lammert, and Crist (*J. Amer. Chem. Soc.* **46**, 1170 (1924)) have shown that acetophenone is decomposed with the formation of benzoic acid in light, and that when salts such as sodium iodide are present iodine is liberated.

Recently, Leighton and Forbes (*J. Amer. Chem. Soc.* **51**, 3549 (1929)) have studied the decomposition of benzoquinone in aqueous and alcoholic solutions in presence of monochromatic radiations from a mercury vapour lamp. The quantum yield is very small (0.045) in wavelength 5770 Å, and reaches its constant value at 4350 Å, and remains at this value throughout the remainder of the first and the whole of the second absorption bands. In alcohol the quantum yield is independent of quinone concentration, and is equal to 0.5 at 25°. The temperature coefficient of the reaction for a 10° rise is nearly unity.

Light (*Z. physik. Chem.* **122**, 414 (1926)) has observed a disappearance of fine structure with benzoquinone vapour at about 3100 Å, which lies in the second absorption band. According to the ideas developed by Henri, this indicates a pre-dissociation or activation which in the presence of a suitable acceptor can cause photochemical change. Light's measurements indicate an incipient disappearance of fine structure at about 4500 Å in the first absorption band, which apparently corresponds with the photochemical threshold in alcoholic solutions (Also compare Ciamician and Silber *Ber.* **19**, 2899 (1886); **34**, 1530 (1901); Hartley and L. Ward, *J. Chem. Soc.* **95**, 34 (1909)).

Bhatnagar, Dunnicliff, and Ali (*J. Indian Chem. Soc.* **4**, 229 (1927)) have shown that the production of colour and precipitates in concentrated solutions of ammonium thiocyanate is due to oxidation by air and catalysis by light. It is suggested that the red colour is due to cyanogen sulphide, formed by the oxidation of thiocyanic acid produced by hydrolysis of the ammonium salt.

Schweckendiek (*Dissertation, Giessen* (1927)) has stated that guaiaconic acid, like guaiaretic acid, is sensitive to light, the sensitivity being increased by the addition of collodion, zapon lacquer, or a solution of sulphur in carbon disulphide.

Gaffron (*Biochem. Z.* **179**, 157 (1926)) has observed that blood serum in presence of small amounts of various porphyrins, chlorophyll, and certain dyes, absorbs large amounts of oxygen in light with simultaneous evolution of carbon dioxide and formation of ammonia. The rate of photo-oxidation is accelerated considerably by the presence of bile salts. Photo-oxidation of tyrosine and phenol takes place readily in presence of an equivalent amount of sodium hydroxide. In the photo-oxidation of uric acid, 1 mol of oxygen is absorbed, and an equivalent amount of carbon dioxide is evolved. Gaffron (*Ber.* **60**, B, 2229 (1927)) has shown that when a solution of chlorophyll in amylamine is exposed to light and then placed in the dark, the quantity of peroxidic oxygen found is approximately equal to the molecular oxygen absorbed. The photochemical action depends greatly on the nature of the solvent used.

Eggert (with W. Schroter) (*Z. Elektrochem.* **34**, 602 (1928)) has investigated the photochemical decomposition of the diazo compounds derived from 2 amino- α -naphthol-4 sulphonic acid and *p*-aminodiphenylamine by measuring the rate of liberation of nitrogen. The quantum yield (0.35) is stated to be independent of the intensity and wavelength of the light, and of the temperature and concentration of the diazo-solution. The same quantum yield is obtained with the solid compounds.

Ramsperger (*J. Amer. Chem. Soc.* **49**, 912 (1927); **50**, 123 (1928); *Proc. Nat. Acad. Science* **13**, 849 (1927)) has investigated the photochemical decomposition of azomethane and azoisopropane in ultra-violet light. The ultra-violet absorption curve of azomethane is maximal at about 3390 Å. and minimal at 2700 Å. Two molecules of the gas were decomposed for each light quantum (wavelength 3660 Å) absorbed, and this may be due to the activation of an azomethane molecule by transference of energy from a newly formed ethane molecule. The temperature coefficient is 1.02 for 10° rise.

Very recently, Villars (*J. Amer. Chem. Soc.* **52**, 61 (1930)) has shown that the brown coloration which hydrogen cyanide acquires on exposing it to radiations from a hydrogen discharge tube, built according to the method of Bay and Steiner (*Z. Physik.* **45**, 337 (1927)), is more likely due to the initial decomposition of HCN into H and CN, and a subsequent polymerization of cyanogen to paracyanogen, than to a direct polymerization of hydrogen cyanide to (HCN)₃. The fact that hydrogen cyanide shows no absorption between 2800 to 2100 Å supports the view that hydrogen cyanide is not an "ionic" molecule, that is, it is incapable of being dissociated into ions by sufficient vibrational energy.

Norrish and Griffiths (*J. Chem. Soc.* 2829 (1929)) have shown that in the photochemical decomposition of gaseous glyoxal in a 3000 c. p. mercury vapour lamp, the most active radiation has the wavelength 3650 Å. The pressure-time curves conform approximately to the bimolecular formula with respect to glyoxal. The final pressure even after prolonged heating is never exactly half the initial, as would be expected from the equation $2 \text{C}_2\text{H}_2\text{O}_2 = \text{CO} + \text{C}_3\text{H}_4\text{O}_3 \rightarrow \text{polymerized product}$. A secondary reaction $\text{C}_2\text{H}_2\text{O}_2 = 2 \text{CO} + \text{H}_2$ probably occurs to a small extent. There is no thermal dissociation.

Pierce, Leviton, and W. A. Noyes Jr. (*J. Amer. Chem. Soc.* **51**, 80 (1929)) have shown that the early stages in the photo-decomposition of malonic acid lead, almost exclusively, to the formation of carbon dioxide and acetic acid, both in presence and in absence of uranyl sulphate as a photo-catalyst. The quantum efficiency of the catalyzed reaction appears to be smaller than that of the uncatalyzed reaction. In presence of radiation from a mercury arc lamp, the velocity of decomposition increases with addition of uranyl sulphate, and approaches a practically constant value, whereas with a constant catalyst the rate of decomposition of malonic acid is proportional to the cube root of the acid concentration. These authors did not find any evidence of the presence of a complex molecule which is light-sensitive, although Ghosh and co-workers (*J. Indian Chem. Soc.* **4**, 353 (1927)) supported

the view that intermediate light-sensitive complexes are formed in mixtures of malonic acid and uranyl nitrate.

De Hemptinne (*Ann. Soc. Sci. Bruxelles*, **48**, B, 98 (1928); *J. Phys. Radium* (VI) **9**, 357 (1928)) has shown that the photolysis of benzaldehyde by radiations shorter than 2600 Å takes place as follows:



the hydrogen then reacting with the phenyl group to form benzene. The energy necessary for this decomposition is calculated to be 115,780 gram-calories corresponding with radiations of wavelength 2461 Å. This is the wavelength at which the total absorption band of the benzaldehyde spectrum begins. The author has also investigated the decomposition of benzaldehyde vapour at 0.2 mm. pressure by ultra-violet light. Only wavelengths corresponding with the total absorption portions of the benzaldehyde spectrum are effective in the photochemical decomposition. With rise of temperature the intensities of the bands gradually decrease, until at 200° a continuous spectrum results, which in turn disappears at 400°. Below this temperature the photolysis is reversible. Between 400° and 500° benzaldehyde begins to decompose thermally and irreversibly. The decrease in the light energy necessary for decomposition at the higher temperatures is of the same order of magnitude as the increase in the vibrational energy of the benzaldehyde molecule, as calculated from the variation of the specific heat with the temperature.

Plisov (*Gazzetta* **59**, 200 (1929)) has shown that the influence of light is more pronounced in the combination of aniline with benzyl chloride than in the case of o-toluidine and benzyl chloride. In the former case, the yield in 3 hours increased from 15% for the dark reaction to 82% when the mixture was illuminated in a quartz vessel by an electric arc.

Recently, Puxeddu (*ibid.* **59**, 160 (1929)) has investigated the effect of sunlight on solutions of mercuric, lead, and titanous chlorides in anhydrous ether, exposed for long periods in sealed tubes. Little photochemical action was observed with lead chloride solutions, but with mercuric chloride solutions, after 5½ months, a greyish white precipitate separated, which on heating was found to consist of mercury and calomel. In the solution, the presence of aldehydes and chloro-compounds, as well as of hydrogen chloride, was detected. Photochemical action was much more rapid in the titanous chloride solution. In two or three days, the original clear yellow solution became deep brown, and later, clear green in colour.

Seyewetz and Mounier (*Compt. rend.* **186**, 953 (1928)) have investigated the decomposition of diazocompounds in ultra-violet light, and the influence of substituents; the p_H values of the media have also been studied. In presence of acids, the diazo salt solutions are very sensitive to light but relatively stable to heat, whilst in alkaline solutions the reverse is true.

Ghosh and Mukherji (*J. Indian Chem. Soc.* **4**, 343 (1927)) have shown that in the photochemical oxidation of leucomalachite green by uranyl nitrate in monochloroacetic acid solution, the velocity varies directly as the intensity of the light and the concentration of uranyl nitrate. The region 4780 — 4100 Å is most suitable for this reaction, and the quantum yield is less than unity while the temperature coefficient of the reaction is practically unity.

Ariga (*Bull. Chem. Soc. Japan* **2**, 65 (1927)) has found that the rate of decolorization of malachite green solutions when alkali is added to them follows the unimolecular formula. When the colourless solution is exposed to the light from a mercury vapour lamp it regains its colour, and this reaction also follows the unimolecular formula and is proportional to the light intensity while the temperature coefficient of the light reaction is unity. Intense sunlight has the same effect as the light from a mercury lamp.

Ghosh and colleagues (*J. Indian Chem. Soc.* **2**, 241 (1925); **3**, 273 (1926)) have studied the transformation of allo-cinnamylidene acetic acid into the normal form, with iodine as a photocatalyst, in methyl alcohol and chloroform solutions. Equilibrium is attained when 90% conversion has been effected, this value being independent of the concentration of the iodine and the intensity of the light, and almost independent of temperature. Nearly 4.23×10^2 molecules are transformed per quantum of light absorbed. The temperature coefficient of the transformation is nearly unity.

Ghosh and Basu (*J. Indian Chem. Soc.* **4**, 375 (1927)) have shown that the photo-bromination of ethyl m-nitrobenzylidene malonate to the dibromide in carbon tetrachloride solution is reversible. The equilibrium constant varies with the intensity of the light, and the ratio of the equilibrium constants measured equals the square root of the ratio of the intensities of incident light. The equilibrium constant is slightly affected by temperature, rise of temperature causing an increase in the concentration of the dibromide. The velocity of the direct action is not affected by the concentrations of ester, bromine, or dibromide. The temperature coefficient for a 10° rise is 2.4. More than one quantum of energy is necessary for the production of one mol of the dibromide.

Ghosh, Basu, and Bhattacharya (*J. Indian Chem. Soc.* **5**, 183 (1928)) have shown that the addition of bromine to ethyl m-nitrobenzylidene malonate, under the influence of light in carbon disulphide solution, is analogous to the reaction in carbon tetrachloride. The equilibrium constant is approximately proportional to the square root of the intensity of incident light. The velocity in the initial stage is proportional to the concentration of bromine, and increases considerably with increase in the concentration of the ester. The values for the equilibrium constant and velocity are about seven times as great in carbon tetrachloride as in carbon disulphide.

Recently, Meyer and Pukall (*Z. phys. Chem.* **145**, 360 (1929)) have studied the rates of bromination in chloroform solution of the all-cinnamic and trans-cinnamic acids. The effect of yellow light in accelerating the reaction in the case of allocinnamic acid is only $\frac{1}{8}$ of that obtained with the trans-acid.

Basu (*J. Indian Chem. Soc.* **6**, 691 (1929)) has shown that the reaction between chlorine and cyclohexane dissolved in CCl_4 , in presence of white or monochromatic light, is unimolecular with respect to chlorine. The velocity is directly proportional to the light intensity, is independent of the chlorine, and increases slightly with the concentration of the cyclohexane. The quantum yield is 19 at 4360 Å, 30 at 4040 Å, and 41 at 3660 Å. The temperature coefficients for the same wavelengths are 1.5, 1.29, and 1.26 respectively.

Böeseken and Langedijk (*Proc. K. Akad. Wetensch. Amsterdam* **30**, 189 (1927)) have shown that in presence of radiations of wavelengths 4000–4100 Å certain aromatic mono- and aliphatic α -di-ketones can behave as photocatalysts in the oxidation of alcohols to the corresponding aldehydes. Visser (*Rec. trav. chim.* **47**, 1037 (1928)) has explained the photocatalytic action of benzo-phenone in the photo-oxidation of alcohols from the view point of the photo-electric emission of electrons from benzophenone.

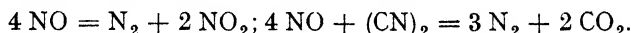
Warburg and Negelein (*Naturwiss.* **16**, 387, 856 (1928); *Biochem. Z.* **200**, 414 (1928); **204**, 495 (1929)) have investigated the influence of pressure of carbon monoxide, of temperature, and of the wavelength of light on the photo-dissociation of iron carbonyl compounds (carbon monoxide-haemochromogen, carbon monoxide-ferrocysteine). The light absorptions of both these compounds have been determined, and it has been observed that the Einstein law of photochemical equivalence is applicable to these reactions.

The photochemical decomposition of iron carbonyl with ultra-violet radiation agrees with the equation $\text{Fe(CO)}_5 + 1 h\nu = \text{Fe(CO)}_4 + \text{CO}$.

Carbon monoxide is likewise set free by the action of light on the haemoglobin "carbonyl", but on account of the high velocity of the back reaction no quantitative work is possible. The course of the photochemical change with carbon monoxide-pyridine-haemin and carbon monoxide-ferrocysteine follows the equations $2 \text{Fe}(\text{CO}) + 1 h\nu = 2 \text{Fe} + 2 \text{CO}$ and $2 \text{Fe}(\text{CO})_2 + 1 h\nu = 2 \text{Fe} + 4 \text{CO}$ respectively, i.e. in both cases two atoms of "carbonyl" iron are set free per light quantum absorbed.

According to Eyber (*Z. physikal. Chem.* **144**, 1 (1929)) the photochemical decomposition of iron penta-carbonyl can be represented by the following equation: $2 \text{Fe}(\text{CO})_5 = \text{Fe}_2(\text{CO})_9 + \text{CO}$. The quantum yield at 20° for radiations of wavelength 4000 \AA is two. The velocity is directly proportional to the concentration of the vapour and to the light intensity.

Norrish and Smith (*Trans. Faraday Soc.* **24**, 620 (1928)) have shown that two reactions, of which the former is about six times as extensive as the latter, occur when mixtures of nitric oxide and cyanogen, each at $\frac{1}{2} - \frac{1}{3}$ atmospheric pressure, are irradiated by ultra-violet light of wavelength $3600-2200 \text{ \AA}$. The reactions are:



In the former reaction, cyanogen acts as catalyst, but neither reaction occurs in the absence of a trace of oxygen, and therefore of nitrogen peroxide. The total reaction is autocatalytic as a result of the accumulation of nitrogen peroxide. There are certain side reactions as well.

PHOTOPOLYMERIZATION.

Reaction	Reference
The reactions occur in ultra-violet light except when otherwise stated	
Acetylene \rightarrow solid yellow polymer, no benzene is observed	Berthelot and Gaudechon, (<i>Compt. rend.</i> 150 , 1169 (1910)); Mathews and Dewey (<i>ibid.</i> 151 , 395 (1910))
Allylene \rightarrow solid white polymer	Berthelot (<i>Travaux scientifiques. Paris</i> (1917), p. 130)
Ethylene \rightarrow Syrupy liquid boiling below 100° , resembling caprylene	do.
Cyanogen \rightarrow Paracyanogen (solid) (in presence of oxygen, cyanogen undergoes oxidation to CO_2 and N_2). Methane and other saturated hydrocarbons are not modified by ultra-violet rays, but in presence of oxygen highly con-	do.

PHOTOPOLYMERIZATION (Continued).

Reaction	Reference
densed paraffins, unattacked by boiling nitric or sulphuric acid, are formed. It is suggested that methane given out in volcanic eruptions is absorbed in this way and petroleum formed in nature. Thiocyanogen in carbon tetrachloride solution polymerizes readily in sunlight	Berthelot (<i>Travaux scientifiques. Paris</i> (1917), p. 130)) Kaufmann and Liepe (<i>Ber.</i> 56 B , 2514 (1923))
Acrolein \rightarrow becomes solid in 90 minutes exposure to ultra-violet light from a mercury vapour lamp. In sunlight the change is slow. In presence of oxygen, partial photochemical oxidation takes place	Moureu, Murat, and Tampier (<i>Compt. rend.</i> 172 , 1267 (1921)); Moureu, Dufraisse, and Bodoche (<i>Bull. Soc. chim.</i> 35 1572, 1591 (1925))
Diphenylene ethylene \rightarrow polymerizes and becomes insoluble in ether on 10 minutes' exposure to mercury arc	Ferrer (<i>Chem. Abs.</i> 17 , 3177 (1923))
Vinyl chloride ($\text{CH}_2 : \text{CHCl}$) \rightarrow amorphous insoluble solid (Specific gravity = 1.41)	Baumann (<i>Annalen</i> 163 , 317)
Vinyl bromide ($\text{CH}_2 : \text{CHBr}$) \rightarrow amorphous insoluble solid (specific gravity = 2.07)	
Vinyl esters form celluloid-like solids on illumination	Klatte and Tollett (<i>U. S. Patent</i> 1241738 Oct. 2 (1917))
Solution of vinyl chloride $\text{CH}_2 : \text{CHCl} \rightarrow (\text{CH}_2\text{CH} \cdot \text{Cl})_{16}$ in extreme ultra-violet radiations from a mercury arc. This polymerization is utilized for synthetic rubber formation	Plotnikoff (<i>Z. wiss. Phot.</i> 21 , 117 (1922))
Vinyl bromide \rightarrow polymerization to α , β , and γ "caouprene bromide" in sunlight	Ostromuiskenski (<i>J. Russ. Phys. Chem. Soc.</i> 44 , 204 (1912))
p-Vinyl anisole \rightarrow polymer in sunlight	Stobbe and Toepfer (<i>Ber.</i> 57 , 484 (1924))
γ -Phenylvinyl acetic acid \rightarrow resinification	Stoermer and Stockmann (<i>Ber.</i> 47 , 1793 (1914))
β -Mesityloxidoxalic esters \rightarrow dimeric forms	Federlin (<i>Annalen</i> 356 , 261 (1907))
Indene \rightarrow polymerization in ultra-violet rays	Stobbe and Farber (<i>Ber.</i> 57 , 1845 (1924))
Stilbene \rightarrow polymerization in ultra-violet rays (in benzene solution)	Stobbe (<i>Ber.</i> 47 , 2701 (1914))
Styrene \rightarrow metastyrene	do.
Oils in the process of drying in daylight undergo polymerization along with oxidation. This is accelerated by ultra-violet light	Marcusson (<i>Z. angew. Chem.</i> 35 , 543 (1922))

The polymerization of anthracene to dianthracene in light, first investigated by Luther and Weigert, has already been discussed in detail. The photo-polymerization of vinyl esters may have some industrial applications. Klatte and Tollett have reported that this photo-polymerization is accelerated by benzoyl peroxide, ozonides, and anhydrides of organic acids containing percarbonates, perborates, and silver oxide. The products are colourless, transparent, and odourless solids, which can be turned, and cut or planed. They become plastic in hot water, and hard again on cooling. Kuhl has reported the formation of a fire-proof substitute for celluloid by the exposure of vinyl acetate and chloracetate to ultra-violet rays. Lord Rayleigh (*Nature* **127**, 645 (1928)) has shown that celluloid stained with malachite green is converted by exposure to sunlight or by heating into a material which transmits only deep red and infra-red rays. Cofman and De Vore (*Nature* **123**, 87 (1929)) have suggested that this change is apparently due to the liberation of oxides of nitrogen. The wavelength most effective in the acid decomposition of cellulose nitrate is 3100 Å.

De Vore, Pfund, and Cofman (*J. Phys. Chem.* **33**, 1836 (1929)) have observed that thin films (0.001 mm.) of cellulose nitrate decompose in light, the mercury arc spectrum from 1900 to 2600 Å being the most effective light source.

Reinicke (*Z. angew. Chem.* **41**, 1144 (1928)) has shown that carefully dried and purified acetylene remains unchanged in sunlight. Polymerization occurs if the gas is exposed to the light from a mercury vapour lamp, but radiations of wavelengths shorter than 3000 Å appear to be active. Oxygen and moisture hinder the polymerization.

PHOTOCHEMICAL SYNTHESIS

Reacting substances	Products formed	Reference
Acetic acid and aniline (equimolecular proportions)	Theoretical yield of acetanilide after 24 hours irradiation with ultra-violet light	Stoermer and Robert (<i>Ber.</i> 55 B, 1030 (1922))
Propionic acid and aniline	Propionanilide-yield 65%	
Ammonium acetate in excess of ammonium hydroxide	Acetamide-yield 5%	
Benzaldehyde and oxygen at the temperature of solid carbon dioxide	Benzoic acid along with the peroxide in ultra-violet rays	Suida (<i>Ber.</i> 47 , 471 (1914))

PHOTOCHEMICAL SYNTHESIS (Continued).

Reacting substances	Products formed	Reference
Benzaldehyde (1 mol), acetic anhydride (3 mols) and oxygen at atmospheric pressure	Benzoyl acetyl peroxide accelerated by light	Jorissen and Ringer (<i>Chem. Zentr.</i> 76 , 1, 817 (1905))
Aldehydes, oxygen, or oxygen-containing gases at low temperatures	Peracids	British Patent 16,849, July 22 (1913)
Ketones and anhydrous alcohols exposed to ultra-violet light	Pinacols	Böeseken and Cohen (<i>Proc. k. Akad. Wetensch. Amsterdam</i> 17 , 849 (1914)); Cohen (<i>Rec. trav. chim.</i> 39 , 243 (1920))
Isoeugenol exposed to ultra-violet rays in air	Vanillin	Wood (<i>Chem. and Met. Eng.</i> 28 , 399 (1923))
Eugenol exposed to ultra-violet rays in air at a temperature 50—60°	Vanillin (95% yield)	Genthe & Co. (<i>D. R. Patent</i> 224,071)
Methyl alcohol and potassium nitrite in diffused daylight or ultra-violet light	Potassium form-hydroxamate	Baudisch (<i>Ber.</i> 44 , 1009 (1911); 49 , 1176 (1916); 53 , 193 (1920))
Unsaturated hydrocarbons and sulphur dioxide exposed to sunlight or ultra-violet rays	Additive products with butylene ($C_4H_8SO_2$) _n produced. Similar compounds of a horny or glassy white solid consistency, not easily inflammable, used for varnishes, transparent films, etc. obtained with amylene, ethylene, etc.	Mathews & Elder (British Patent 11,635, May 11 (1914))
Phenylacetic acid, benzophenone and anhydrous benzene when exposed to sunlight for 112 days	α - and $\beta\beta$ -triphenyl lactic acid crystals were obtained	De Fazi (<i>Chem. Zent.</i> 1 , 2174 (1928))
Raw turpentine when exposed to ultra-violet rays and air	α - and β -pinenes are formed	Dedichen and Halse (<i>U. S. Patent</i> 1,253,793 January 5 (1918))
Alcoholic solutions of transcyclopentane 1:2 carboxylic acid in uvial lamp light	Mono- and di-esters	Stoermer and Ladewig (<i>Ber.</i> 47 , 1803 (1914))

PHOTOCHEMICAL SYNTHESIS (Continued).

Reacting substances	Products formed	Reference
Ammonia and carbon monoxide combine in ultra-violet light	Formamide	Berthelot and Gaudechon (<i>Compt. rend.</i> 155 , 207 (1912))
Phenylhydrazine and aromatic ketones	l-phenyl pyrazolines	Muffat and Heitz (<i>Ber.</i> 51 , 1457 (1918))

It will be evident from the foregoing table that numerous organic compounds have been synthesized by the action of light.

PHOTOCHEMICAL REARRANGEMENTS.

Reaction	Reference
o-Nitrobenzaldehyde \rightarrow o-nitrosobenzoic acid	Weigert and Kummerer (<i>Ber.</i> 46 , 1207 (1913))
Cinnamylidene malonic acid \rightarrow Diphenyl tetra-methylenediethylidicarboxylic acid	Hartley and Scott (<i>J. Chem. Soc.</i> 125 , 1233 (1924))
Fumaric acid \rightarrow Maleic acid	Kailan (<i>Z. Physik. Chem.</i> 87 , 333 (1914))
Crotonic acid \rightarrow Isocrotonic acid	Stoermer and Robert (<i>Ber.</i> 55 B , 1030 (1922))
Coumaric acids undergo stereo-isomeric change, the stable forms passing into labile forms in ultra-violet light	Stoermer (<i>Ber.</i> 42 , 4865 (1909); 44 , 637 (1911))
Cinnamic acids in solution or in molten condition undergo isomeric change in radiations 2700—3200 Å. In sunlight the changes are slow	Stobbe and coworkers (<i>Ber.</i> 52 , 666 (1919); 55 B. , 2225 (1922))
n-Chloracetanilide undergoes isomeric change to Para-chloracetanilide in light: $\text{CH}_3\text{CONClC}_6\text{H}_5 \rightarrow \text{CH}_3\text{CONHC}_6\text{H}_4\text{Cl}$	Chattaway and Orton (<i>J. Chem. Soc.</i> 81 , 200 (1902)); Blanksma (<i>Rec. trav. chim. Pays-Bas</i> 22 , 290 (1903)); Mathews and Williamson (<i>J. Amer. Chem. Soc.</i> 45 , 2574 (1923))
Benzoyl phenylethylene oxide	Bodfross (<i>Ber.</i> 51 , 214 (1918))
Benzoyl-m-nitrophenyl ethylene oxide	
Benzoyl-p-chlorophenyl ethylene oxide	
These substances undergo rearrangements in ultra-violet light to α -hydroxystyryl ketones from methyl alcoholic solutions	

PHOTOCHEMICAL REARRANGEMENTS (Continued).

Reaction	Reference
α -Methyl- β -phenyl-indone in benzene solution changes to dimethyl-diphenyltruxone in ultra-violet light	De Fazi (<i>Gazz. Chim. ital.</i> 54 , 85 (1924))
Anti-aldoximes \rightarrow Syn-isomerides in ultra-violet light	Ciamician and Silber (<i>Ber.</i> 36 , 4268 (1903)); Brady and McHugh (<i>J. Chem. Soc.</i> 125 , 547 (1924))
Some semicarbazones yield stereoisomers in ultra-violet radiations	Wilson and Macaulay (<i>J. Chem. Soc.</i> 125 , 841 (1924))
Yellow methyl and ethyl esters of benzoyl acrylic acid are transformed to colourless stereoisomeric esters in sunlight.	Rice (<i>J. Amer. Chem. Soc.</i> 45 , 222 (1913); 46 , 214, 2319 (1924))
The reverse transformation of the colourless esters to yellow takes place in sunlight in solutions containing bromine or iodine in traces. Other derivatives behave in the same way.	
Methyl benzalpyruvate when exposed to sunlight in the dry state forms a polymeric ester; in benzene solutions isomerization and subsequent polymerization take place	Reimer (<i>J. Amer. Chem. Soc.</i> 47 , 783 (1924))
Methyl salicylate becomes coloured on exposure to air and sunlight. Similar behaviour is observed with o-m- and p-cresols, esters of the three hydroxybenzoic acids, gentisic acid and its esters	Stoermer and Ladewig (<i>Ber.</i> 47 , 1803 (1914)); Gibbs, Williams, and Pratt (<i>Philippine J. Sci.</i> 7 (2) 79 (1912))
Isobutyl bromide when exposed to ultra-violet rays forms tertiary butyl bromide, and propyl bromide changes to isopropyl bromide without dissociation	(Mme.) Ramart-Lucas and F. Salmon-Legagneur (<i>Compt. rend.</i> 186 , 39 (1928))

Porter and Wilbur (*J. Amer. Chem. Soc.* **49**, 2145 (1927)) have measured the ultra-violet absorption spectra of acetyl chloroaminobenzene and its isomeride, p-chloroacetanilide. Conversion into the isomeride occurs in the solid state in the radiation of a mercury vapour lamp, and also at 100°. The change is rapid above the melting point.

CHAPTER XIX.

Influence of Temperature on Photochemical Reactions.

Marcelin Berthelot (1865) was the first to state that the influence of temperature on photochemical reactions would be similar to that of high temperatures on chemical reactions. G. Lemoine (*Ann. Chim. Phys.* **6**, 448 (1855)) reported from his experiments on the influence of sunlight on the reaction between ferric chloride and oxalic acid, that the temperature coefficient of the reaction for a 10° rise was 1.2. In other words, the temperature coefficient approached unity. D. Berthelot (*Compt. rend.* **160**, 440 (1915)) obtained the value 1.01 for the same reaction in sunlight, and 1.03 in the decomposition of laevulose in the light of a mercury vapour lamp.

Goldberg (*Z. physik. Chem.* **41**, 1 (1902); *Z. wiss. Phot.* **4**, 56 (1906)) pointed out the fact that temperature coefficients of photochemical reactions are smaller than those of thermal reactions. In recent years numerous reactions have been investigated, and the values of their temperature coefficients obtained still justify the truth of the statement that the temperature coefficients of the photochemical reactions are as a rule less than of those taking place in the dark.

In several publications from the author's laboratories it has been shown that the temperature coefficient of a photochemical reaction is always less than that of the same reaction taking place in the dark. Moreover, it has been proved with numerous photochemical reactions taking place in radiations of different wavelengths, that the temperature coefficient of a reaction depends on the acceleration of the reaction by the absorption of radiation. The greater the acceleration of a reaction on illumination, the smaller is the value of its temperature coefficient. This relation has been found to hold good rigidly with more than 40 photochemical reactions investigated in the author's laboratory.

From the researches of Slator (*Z. physik. Chem.* **45**, 513 (1903)) on the chlorination of benzene in the presence of several catalysts, and of light, we get the following interesting results:

Catalyst	ICl	SnCl ₄	FeCl ₃	Light
Temp. Coeff.	1.05	1.5	2.5	1.5

Of the three positive chemical catalysts used in this reaction the order of efficiency is the following: $\text{ICl} > \text{SnCl}_4 > \text{FeCl}_3$. It is clear that the greater the acceleration produced by a given catalyst, the smaller is the value of the temperature coefficient. The temperature coefficient of the reaction with the strong positive catalyst iodine chloride in the dark is much smaller than that of the reaction carried out in light without any chemical catalyst. A strongly catalyzed reaction in the dark may have a very small temperature coefficient, just like a photochemical reaction.

Hitherto the opinion has been generally held that in light the temperature coefficient of photochemical reactions should be unity. We have shown in many cases that the temperature coefficient of a reaction occurring in light is much greater than unity, but smaller than that of the reaction in the dark, provided light accelerates the change. The diminution of the temperature coefficient depends on the acceleration of the reaction in light. Let us consider the case of the oxidation of potassium oxalate by iodine in light, first investigated by us. The temperature coefficient of the reaction in the dark has the high value 7.2 for 10° rise; in diffused light the reaction is accelerated, and the temperature coefficient is 3.4, whilst in tropical sunlight the reaction is enormously accelerated and the temperature coefficient is 2.68. Hence the greater the acceleration of a reaction by light, the greater is the fall in temperature coefficient. It is clear, therefore, that a typical photochemical reaction such as the oxidation of potassium oxalate by iodine may have a temperature coefficient much greater than unity. Most of the photochemical reactions ordinarily investigated take place also in the dark, but at a much smaller speed than in light. In other words, in presence of light the number of active molecules in the reacting system is greatly increased, and that is why the speed of the reaction is much greater. If light activates most of the molecules there will not be any marked increase in activation with increase of temperature. Hence the temperature coefficient in such cases should be either unity or very nearly unity. On the other hand, if light is unable to activate a large number of the reactant molecules, increase of temperature would lead to the activation of more molecules. In such cases the temperature coefficient may have much larger value than unity. When a reaction is ideally photochemical, that is, when in the absence of light the chemical change does not take place at all, we should expect the temperature coefficient to be unity, because in such cases increase of temperature does not bring about the activation of molecules.

The above views and conclusions of the writer are in agreement with the results obtained by Lind and Livingston (*J. Amer. Chem. Soc.* **52**, 593 (1930)) on the temperature coefficient of the synthesis of hydrogen chloride by light and by α -radiation. These authors have found that in white light the temperature coefficient varies with the sensitivity of the reacting mixture. It has also been shown that the temperature coefficient has a value about 10% higher in green light than in white light. The radiochemical synthesis has practically the same temperature coefficient as that of the photosynthesis in white light. Their experimental results show that the greater the acceleration of the reaction by light or α -radiations, the smaller is the temperature coefficient.

The view that the temperature coefficients of photochemical reactions are relatively small has been regarded as incorrect by Bancroft and Allen (*Proc. Nat. Acad.* **15**, 445 (1929)).

In the following table (p. 312—319) the existing literature on photochemical reactions has been summarized.

The first attempt to interpret the observed temperature coefficients was undertaken by Plotnikoff (*Z. physik. Chem.* **78**, 573 (1911)) who suggested a classification of the values of the temperature coefficients amongst three groups. To the first group he assigned those averaging 1.04 for ten degrees temperature change, to the second those with values close to 1.2, and to the third those close to 1.4. In the opinion of Plotnikoff the deviations from these averages are due to experimental errors. He suggested that these values of temperature coefficients depend on the electronic arrangement in the atoms of the reacting substances, and supposed them to remain unchanged in most photochemical reactions. By a glance at the following table it will be clear that neither the classification in three groups, nor constancy of temperature coefficient for the reactions of the same light-sensitive atom are in accord with the actually observed relations.

Bodenstein (*Z. physik. Chem.* **85**, 318 (1913)) suggested that for the occurrence of a photochemical reaction it is necessary to have not only the activation of the light absorbing component which should be practically independent of the temperature of the reacting substances, but also an activation of the other reactant. According to Bodenstein, the latter must be caused by the energy of thermal agitation in a manner identical with that of thermal reaction, thereby promoting the sensitivity of the photochemical reaction to changes of temperature. It follows, therefore, that the temperature coefficient of a purely

THE TEMPERATURE COEFFICIENTS OF PHOTOCHEMICAL REACTIONS.

I. Gases.

Reactions	Temperature Coefficients	Temperature Intervals °	Illumination	Reference
$2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$	1.00	150—175	Hg arc quartz	Bodenstein and Lieneweg (<i>Z. physik. Chem.</i> 119 , 123, (1926))
$2 \text{NOCl} \rightarrow 2 \text{NO} + \text{Cl}_2$	1.00	0—78	Incandescent lamp glass	Kiss (<i>Rec. trav. chim.</i> 42 , 665 (1923))
Photosensitizations by excited Hg atoms	1.00	25—70	2536 Å	Marshall (<i>J. Phys. Chem.</i> 30 , 1078 (1926))
$2 \text{Cl}_2\text{O} \rightarrow 2 \text{Cl}_2 + \text{O}_2$	1.09	10—40	Hg arc glass	Kistiakowsky (<i>Z. physik. Chem.</i> 116 , 371 (1925))
$2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$	1.04	150—240	Hg arc quartz	Coehn and Grote (<i>Nernst Festschrift</i> 136 (1912))
$2 \text{O}_3 + \text{Cl}_2 \rightarrow 3 \text{O}_2 + \text{Cl}_2$	1.17	16—25	Hg arc glass	Weigert (<i>Z. Elektro.</i> 14 , 591 (1908))
$2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$	1.06	131—228	Hg arc quartz	Andrejeff (<i>J. Russ. Chem. Soc.</i> 43 , 1342 (1911))
$2 \text{NH}_3 \rightarrow 3 \text{H}_2 + \text{N}_2$	1.04	18—500	2025—2140 Å	Kuhn (<i>Compt. rend.</i> 178 , 708 (1924))
$3 \text{O}_2 \rightarrow 2 \text{O}_3$	1.00 < 1.00 (less concentration)	—180—18	< 2000 Å	Eucken (<i>Z. physik. Chem.</i> 107 , 436 (1923))
$\text{Cl}_2 + \text{H}_2 \rightarrow 2 \text{HCl}$	1.21	11—60	Sunlight	Bevan (<i>Proc. Camb. Phil. Soc.</i> 12 , 398 (1904))
	1.1	—	Incand. lamp blue filter	Porter, Bordwell, and Lind (<i>J. Amer. Chem. Soc.</i> 48 , 2603 (1926))
	1.29	10—40	White Light	Padoa and col- laborators (<i>Atti Accad. Lincei</i> 25 II, 215 (1916))
	1.50	do.	5500—5300 Å	
	1.31	do.	4900—4700 Å	
	1.21	do.	4600—4400 Å	
	1.17	do.	4000—3500 Å	
$\text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2$	0.88	—	—	Trautz (<i>Z. Elektrochem.</i> 21 , 336 (1915))
$\text{Cl}_2 + \text{CO} \rightarrow \text{COCl}_2$	1.00	18—28	Incand. lamp glass	Bodenstein (<i>Rec. trav. chim.</i> 41 , 585 (1915))
	< 1.00	18—35	Incand. lamp glass	Chapman and Gee (<i>J. Chem. Soc.</i> 99 , 1726 (1911))
$2 \text{O}_3 \rightarrow 3 \text{O}_2$	1.15	18—35	Hg arc quartz	Weigert (<i>Z. physik. Chem.</i> 80 , 78 (1912))
Decomposition of azo-methane	1.02	—	Ultra-violet (3660 Å)	Ramsperger (<i>J. Amer. Chem. Soc.</i> 49 , 912 (1927))

Reactions	Temperature Coefficients	Temperature Intervals °	Illumination	Reference
$2\text{O}_3 \rightarrow 3\text{O}_2$	1.40 1.3 (high concentrations) 1.0 (low conc.)	0—20	Incand. lamp glass 5800—6500 Å	Griffith and McKeown (<i>Trans. Far. Soc.</i> 21 , 597 (1925)) <i>Photochemical processes</i> , by Kistiakowsky (p. 242 (1928))
$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	1.48	160—218	Incand. lamp glass	Bodenstein and Lütke-meyer (<i>Z. physik. Chem.</i> 121 , 127 (1926))

II. Liquids.

$\text{H}_2\text{C}_2\text{O}_4 + \text{VO}_2^+ \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O} + \text{VO}_2^+$	1.00	4—80	Sunlight	Brunner and Kozak (<i>Z. Elektrochem.</i> 17 , 355 (1911))
	1.00	20—100	Sunlight	Bacon (<i>The Philipp J. of Sci.</i> 5 , 281 (1910))
Lactic acid + VO_2^+	1.00	20—30	Carbon arc glass	Bolin (<i>Z. physik. Chem.</i> 87 , 490 (1914))
Quinine + CrO_4^{--}	1.04	20—70	Hg arc thin glass	Goldberg (<i>Z. wiss. Phot.</i> 4 , 61 (1906))
Anthracene-Dianthracene	1.04	75—109	Hg arc glass	Weigert (<i>Ber.</i> 42 , 854 (1909))
β -methyl anthracene \rightarrow di- β -methyldianthracene	1.00	150—160	Hg arc glass	Weigert and Krüger (<i>Z. physik. Chem.</i> 85 , 579 (1913))
$2\text{Fe}^{++} + \text{I}_2 \rightarrow 2\text{Fe}^{+++} + 2\text{I}^-$	< 1.17	25—35	Incand. lamp glass	Rideal and Williams (<i>J. Chem. Soc.</i> 127 , 258 (1926))
$\text{H}_2\text{C}_2\text{O}_4 + 2\text{FeCl}_3 \rightarrow 2\text{CO}_2 + 2\text{FeCl}_2 + 2\text{HCl}$	1.02	3—44	Sunlight	Lemoine (<i>Ann. Chim. Phys.</i> 6 , 448 (1855))
	1.01	2—61	Sunlight	Berthelot (<i>Comp. rend.</i> 160 , 440 (1915))
Decomposition of laevulose	1.03	40—70	Hg arc quartz	Berthelot (<i>ibid.</i>)
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 + \text{C}_2\text{H}_5\text{OH}$	1.02	20—30	Blue light	Plotnikoff (<i>Z. wiss. Phot.</i> 19 , 40 (1919))
$2\text{Co}(\text{C}_2\text{O}_4)_3\text{K}_3 \rightarrow 2\text{CoC}_2\text{O}_4 + 3\text{K}_2\text{C}_2\text{O}_4 + 2\text{CO}_2$	1.06	12—22	Incand. lamp glass	Vranek (<i>Z. Elektrochem.</i> 23 , 336 (1917))
$2\text{HgCl}_2 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{HCl} + 2\text{CO}_2$	1.19	—	Sunlight	Eder and Valenta (<i>Beitr. z. Photochem.</i> 2 , 11 (1904))

Reactions	Temperature Coefficients	Temperature Intervals °	Illumination	Reference
Eder's solution	1.24	—	Sunlight	Eder (<i>Wien. Akad. Ber.</i> 2 (1879))
$2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$	1.50	21—45	Hg arc uviolet glass	Mathews and Curtis (<i>J. Phys. Chem.</i> 18 , 166 (1914))
	1.15	10—30	Hg arc quartz	Tian (<i>Ann. Physik.</i> 5 , 248 (1916))
	1.32	—	Hg arc quartz	Kornfeld (<i>Z. wiss. phot.</i> 21 , 66 (1921))
	1.43	2—25	Hg arc quartz	Anderson and Taylor (<i>J. Amer. Chem. Soc.</i> 45 , 1210 (1924))
$4 \text{HI} + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + 2 \text{I}_2$	1.39	5—50	Hg arc glass	Plotnikoff (<i>Z. physik. Chem.</i> 58 , 214 (1907)); cf. Padua and collaborators (<i>Gazz. Chim. ital.</i> 55 , 87 (1915))
$2 \text{CHI}_3 + 2 \text{O}_2 \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O} + 3 \text{I}_2$	1.42	3—51	Hg arc glass	Plotnikoff (<i>Z. physik. Chem.</i> 75 , 337 (1910))
$2 \text{Cl}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{HCl} + \text{O}_2$	1.4	5—30	Incand. lamp glass	Benrath and Tüchel (<i>Z. wiss. Phot.</i> 13 , 383 (1913))
$\text{Cl}_2 + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$	1.5	6—20	Sunlight	Slator (<i>Z. physik. Chem.</i> 45 , 513 (1903))
$\text{Br}_2 + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}$	1.4	6—19	Hg arc glass	Plotnikoff (<i>Z. physik. Chem.</i> 78 , 579 (1912))
$\text{Br}_2 + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Br} + \text{HBr}$	1.8	—	Sunlight	Bruner and Czernecki (<i>Bull. Ak. Sci. Cracow.</i> (A) 576 (1910))
$\text{Br}_2 + \text{K}_2\text{C}_2\text{O}_4 \rightarrow 2 \text{KBr} + 2 \text{CO}_2$	1.98	0—15	Incand. lamp glass	Berthoud and Bellenot (<i>Helv. Chim. Acta</i> 1 , 307 (1924))
$\text{I}_2 + \text{K}_2\text{C}_2\text{O}_4 \rightarrow 2 \text{KI} + 2 \text{CO}_2$	3.22 } 3.15 }	25—40	Inc.) Red filt. lamp) Blue filt.	do.
Isomerization of diethyl maleate ester	1.26 1.02	21.5—24.5 4—14	4370—5570 Å	Wachholtz (<i>Z. physik. Chem.</i> 125 , 1 (1927))
Bromination of the same	1.07 1.02	do.	do.	do.
Potassium oxalate and bromine	2.67 2.78 3.06 5.61	20—30 20—30 20—30 20—30	1000 W. lamp 5000—4450 Å 5850—5450 Å 7608—7000 Å Dark	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> (1930))

Reaction	Temperature Coefficients	Temperature Intervals °	Illumination	Reference
Rochelle salt and bromine	2.64	20—30	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	2.03	20—30	5850—5450 Å	
	2.08	20—30	7608—7000 Å	
	3.28	20—30	Dark	
Methyl alcohol and bromine	1.99	20—30	Sunlight	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> 176 , 372 (1928))
	2.4	20—30	5000—4450 Å	
	2.34	20—30	5850—5450 Å	
	2.42	20—30	7608—7000 Å	
	2.50	20—30	Dark	
Ethyl alcohol and bromine	1.54	20—30	Sunlight	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> 176 , 372 (1928))
	2.36	20—30	5000—4450 Å	
	2.04	20—30	5850—5450 Å	
	2.67	20—30	7608—7000 Å	
	2.84	20—30	Dark	
Propyl alcohol and bromine	1.6	20—30	Sunlight	Jugol Kishore Verma and Dhar (<i>Z. anorg. u. allg. Chem.</i> 184 , 58 (1929))
	2.15	20—30	5000—4450 Å	
	2.13	20—30	5850—5450 Å	
	2.35	20—30	7608—7000 Å	
	2.93	20—30	Dark	
Isopropyl alcohol and bromine	1.28	20—30	Sunlight	Jugol Kishore Verma and Dhar (<i>Z. anorg. u. allg. Chem.</i> 184 , 58 (1929))
	2.29	20—30	5000—4450 Å	
	2.28	20—30	5850—5450 Å	
	2.31	20—30	7608—7000 Å	
	2.96	20—30	Dark	
Butyl alcohol and bromine	1.17	20—30	Sunlight	Jugol Kishore Verma and Dhar (<i>Z. anorg. u. allg. Chem.</i> 184 , 58 (1929))
	1.70	20—30	5000—4450 Å	
	1.60	20—30	5850—5450 Å	
	1.80	20—30	7608—7000 Å	
	2.8	20—30	Dark	
Potassium oxalate and iodine	3.01	20—30	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	3.2	20—30	5850—5450 Å	
	3.56	20—30	7608—7000 Å	
	7.2	20—30	Dark	
Sodium formate and iodine	3.72	20—30	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	3.83	20—30	5850—5450 Å	
	4.00	20—30	7608—7000 Å	
	4.30	20—30	Dark	
Sodium citrate and iodine	1.46	23—33	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	1.63	23—33	7608—7000 Å	
	1.64	23—33	Dark	

Reaction	Temperature Coefficients	Temperature Intervals °	Illumination	Reference
Ferrous sulphate and iodine	2.61	24.5—34.5	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	2.79	24.5—34.5	5850—5450 Å	
	2.85	24.5—34.5	7608—7000 Å	
	2.92	24.5—34.5	Dark	
Sodium malate and iodine	1.56	30—40	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	1.57	30—40	7608—7000 Å	
	1.61	30—40	Dark	
Sodium tartrate and iodine	2.11	20—30	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 143 (1929))
	2.20	20—30	5850—5450 Å	
	2.26	20—30	7608—7000 Å	
	2.51	20—30	Dark	
Sodium malonate and iodine	1.85	20—30	5000—4450 Å	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> (1930))
	1.90	20—30	5850—5450 Å	
	2.00	20—30	7608—7000 Å	
	2.21	20—30	Dark	
Sodium lactate and iodine	2.02	20—30	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 143 (1929))
	2.11	20—30	5850—5450 Å	
	2.21	20—30	7608—7000 Å	
	2.49	20—30	Dark	
Acetone and iodine	1.77	21—31	Sunlight	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> 176 , 372 (1928))
	2.70	21—31	5000—4450 Å	
	2.82	21—31	5850—5450 Å	
	2.94	21—31	7608—7000 Å	
	3.21	21—31	Dark	
Sodium nitrite and iodine	2.0	30—40	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 7 , 709 (1930))
	2.21	30—40	5850—5450 Å	
	2.29	30—40	7608—7000 Å	
	2.70	30—40	Dark	
Hydroxylamine hydrochloride and iodine	1.45	20—30	White light	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> (1930))
	1.93	20—30	5000—4450 Å	
	2.10	20—30	5850—5450 Å	
	2.23	20—30	7608—7000 Å	
	2.54	20—30	Dark	
Hydrazine hydrochloride and iodine	1.97	25—35	5000—4450 Å	Bhattacharya and Dhar (<i>ibid.</i>)
	2.07	25—35	5850—5450 Å	
	2.18	25—35	7608—7000 Å	
	2.60	25—35	Dark	
Oxidation of iodoform	1.15	29—39	White light	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
Oxidation of neocyanin	1.29	20—30	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 143 (1929))
	1.20	20—30	5850—5450 Å	
	1.12	20—30	7608—7000 Å	

Reaction	Temperature Coefficients	Temperature Intervals °	Illumination	Reference
Oxidation of dicyanin	1.099	30—40	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	1.106	30—40	5850—5450 Å	
	1.056	30—40	7608—7000 Å	
	1.020	25—35	Sunlight	
	1.354	25—35	Dark	
Mercuric chloride and ammonium oxalate in presence of eosin	1.88	36—46	5400 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850, (1929)); compare Padoa and collaborators (<i>Atti Accad. Lincei</i> 24 11, 97 (1915))
	1.65	36—46	4950 Å	
	1.98	36—46	4350 Å	
Iodic acid and oxalic acid	1.68	25—35	White light	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> (1930))
Potassium persulphate and potassium iodide	1.3	20—30	Sunlight	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> 176 , 372 (1928))
	1.5	20—30	5000—4450 Å	
	1.6	20—30	5850—5450 Å	
	1.64	20—30	7608—7000 Å	
	1.95	20—30	Dark	
Oxidation of quinine by chromic acid	1.14	25—35	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	1.39	25—35	5850—5450 Å	
	1.40	25—35	7608—7000 Å	
	1.60	25—35	Dark	
Oxidation of oxalic acid by chromic acid	1.70	20—30	5000—4450 Å	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> 176 , 372 (1928))
	1.65	20—30	5850—5450 Å	
	1.76	20—30	7608—7000 Å	
	1.90	20—30	Dark	
Oxidation of tartaric acid by chromic acid	1.9	22—32	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 143 (1929))
	1.95	22—32	5850—5450 Å	
	2.0	22—32	7608—7000 Å	
	2.13	22—32	Dark	
Oxidation of citric acid by chromic acid	2.59	24—34	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 143 (1929))
	2.66	24—34	5850—5450 Å	
	2.89	24—34	7608—7000 Å	
	3.73	24—34	Dark	
Oxidation of lactic acid by chromic acid	1.62	22—32	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 143 (1929))
	1.70	22—32	5850—5450 Å	
	1.75	22—32	7608—7000 Å	
	1.80	22—32	Dark	
Oxidation of ethyl alcohol by chromic acid	1.02	20—30	4360 Å	Plotnikoff (<i>Z. wiss. Phot.</i> 19 , 40 (1919))
Oxidation of oxalic acid by potassium permanganate	2.78	14.5—24.5	5000—4450 Å	Mukerji and Dhar (<i>J. Phys. Chem.</i> 33 , 850 (1929))
	2.05	14.5—24.5	5850—5450 Å	
	2.4	14.5—24.5	7608—7000 Å	
	3.09	14.5—24.5	Dark	

Reaction	Temperature Co-efficients	Temperature Intervals °	Illumination	Reference
Oxidation of lactic acid by potassium permanganate	1.56	19—29	Sunlight	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> 176 , 372 (1928))
	2.0	19—29	5000—4450 Å	
	2.2	19—29	5850—5450 Å	
	2.3	19—29	7608—7000 Å	
	2.53	19—29	Dark	
Oxidation of tartaric acid by potassium permanganate	1.5	16—26	Sunlight	Bhattacharya and Dhar (<i>ibid.</i>)
	2.0	16—26	5000—4450 Å	
	2.1	16—26	5850—5450 Å	
	2.3	16—26	7608—7000 Å	
	2.5	16—26	Dark	
Oxidation of citric acid by potassium permanganate	2.2	15—25	5000—4450 Å	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> (1930))
	2.3	15—25	5850—5450 Å	
	2.35	15—25	7608—7000 Å	
	2.92	15—25	Dark	
Decomposition of sodium cobaltinitrite	1.64	20—30	Sunlight	Bhattacharya and Dhar (<i>Z. anorg. u. allg. Chem.</i> 176 , 372 (1928))
	2.34	20—30	5000—4450 Å	
	2.50	20—30	5850—5450 Å	
	2.70	20—30	7608—7000 Å	
	3.50	20—30	Dark	
Decomposition of trichloroacetic acid	3.6	75—85	Sunlight	Banerji and Dhar (<i>Z. anorg. u. allg. Chem.</i> 134 , 172 (1924))
	4.29	80—90	Dark	
Decomposition of ferric thiocyanate	2.12	20—30	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 143 (1929))
	2.30	20—30	5850—5450 Å	
	2.50	20—30	7608—7000 Å	
Decomposition of potassium manganio-oxalate	1.3	6—16	4880 Å	Ghosh and Kappanna (<i>J. Indian Chem. Soc.</i> 3 , 127 (1926))
Decomposition of potassium persulphate	1.2	17—27	Sunlight	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 143 (1929))
Hydrolysis of cane sugar	3.2	35—45	5000—4450 Å	Bhattacharya and Dhar (<i>J. Indian Chem. Soc.</i> 6 , 879 (1929))
	3.4	35—45	5850—5450 Å	
	3.7	35—45	7608—7000 Å	
	3.85	35—45	Dark	
Oxalic acid and chlorine	2.3	15—25	5000—4450 Å	Bhattacharya and Dhar (<i>J. Chim. Phys.</i> 26 , 556 (1929))
	2.4	15—25	5850—5450 Å	
	2.5	15—25	7608—7000 Å	
	2.95	15—25	Dark	
Oxidation of leuco malachite green by uranyl nitrate	1.0	22—32	4780—4100 Å	Ghosh and Mukerji (<i>J. Indian Chem. Soc.</i> 4 , 343 (1927))

Reaction	Temperature Coefficients	Temperature Intervals °	Illumination	Reference
Bromination of ethyl m-nitro-benzidene malonate to the dibromide	2.4	25.5—32	Visible light	Ghosh and Basu (<i>J. Indian Chem. Soc.</i> 4 , 375 (1927))
Decomposition of Fehling's solution	1.2	15—25	Carbon arc	Bolin and Linder (<i>Z. physik. Chem.</i> 93 , 721 (1919))
Bromine and tartaric acid	2	24—34	4900—4500 Å	Ghosh and collaborators (<i>J. Indian Chem. Soc.</i> 2 , 165 (1925); 5 , 342, 361 (1928))

III. Solids.

2 AgBr → 2 Ag + Br ₂	1.03	—190—20	Sunlight	Lumière (<i>Comp. rend.</i> 128 , 359, (1899))
		—85—15	Sunlight	Padoa and Mervini (<i>Gazz. Chim. ital.</i> 47 , 288 (1917))
Bleaching of dyes in colloidal films	1.04 1.07	15—80	5700—6000 Å	Schwezooff (<i>Z. wiss. Phot.</i> 9 , 65 (1910))
Phototropic changes: o-tolyl-piperyl-osazone	1.06	—90—10	—	Padoa and Tabellini (<i>Gazz. Chim. ital.</i> 45 , 10 (1915))
p-p-diamido stilbene -o-o-disulphonic acid	1.07	—10—20	—	Padoa and Zazzaroni (<i>R. Acc. Lincei</i> 24 , 828 (1915))
Benzaldehyde phenyl hydrazone	1.06	—80—0	—	Padoa and Miss Minganti (<i>R. Acc. Lincei</i> 22 , 500 (1913))
Salicilidene-β-phenyl hydrazone	1.4	0—10	—	Ibid.
Styral → meta styral	1.34	3—35	Sunlight	Lemoine (<i>Compt. rend.</i> 129 , 717 (1899))
Phototropic change of salicidene-β-naphthylamine	1.39	—	Violet	Padoa and collaborators (<i>Atti Accad. Lincei.</i> 24 , 828 (1915))
	1.45		Blue	
	1.80		Green	
Silver citrate paper	1.07	—85—45	Ultra-violet	Padoa and collaborators (<i>Atti Accad. Lincei.</i> 25 II, 168 (1916))
	1.119		Blue	
Photographic plate sensitized by pinachrom	1.07	—	4360 Å	Compare Plotnikoff "Lehrbuch" 1920
	1.08		5460—5790 Å	

thermal reaction must be higher than that of a photochemical one, because in thermal reactions the activation of both reactants is due to the supply of thermal energy. In this manner, Bodenstein tried to explain the temperature coefficients of the photochemical (1.8) and thermal (4.0) velocities of the bromination of toluene obtained by Bruner and Czernecki (*Bull. Acad. Sci. Cracow (A)*, 576 (1910)).

According to the law of photochemical equivalence, temperature should not have any influence on the velocity of a photochemical reaction. This has actually been observed with certain reactions, and the values of such reactions approach unity; but there are numerous exceptions where the temperature coefficient is much greater than unity.

Recently Tolman (*J. Amer. Chem. Soc.* **42**, 2506 (1920); **45**, 2285 (1923)) attempted a general theoretical treatment of the temperature coefficient of a photochemical reaction based on statistical mechanics and quantum theory. In a unimolecular process the mechanism is regarded as consisting in the absorption of a quantum $h\nu$, which raises the molecule to such an energy level that the reaction is possible. The velocity of such a reaction will be given by the equation:

$$\frac{dC_A}{dt} = K_\nu U_\nu C_A$$

where K_ν is the specific photochemical reaction velocity, i.e. the rate at unit concentration of the reactant A with unit energy density of frequency ν . Tolman derives an expression for K_ν in terms of the probability that a molecule in a given quantum state will acquire a quantum of energy, and of the probability that such a molecule will then undergo the given unimolecular change. Tolman's expression when differentiated with respect to temperature is the following:

$$\frac{\partial \log K_\nu}{\partial t} = \frac{e'' - e'}{KT^2}$$

where e'' is the average energy before activation of the molecules which actually absorb the radiation and react, and e' is the average energy of all the molecules.

For a bimolecular reaction in which only one reactant A of the two reactants A and B is activated by the radiation the following equation is obtained:

$$\frac{\partial \log K_\nu}{\partial t} = \frac{1}{2T} + \frac{e'' - e'}{KT^2}$$

where e'' is the average energy of the pairs of molecules of A and B that actually react, and e' is the average energy of any pair of molecules A and B . The term $\frac{1}{2T}$ arises from the assumption that the number of collisions of the molecules of the gas is proportional to the absolute temperature. To compare these theoretical equations with experimental results it is necessary to make the following transformations:

$$r = \frac{K_{t+10}}{K_t}$$

$$\frac{\partial \log K_v}{\partial t} = \frac{K_{t+10} - K_t}{10 \left(\frac{K_{t+10} + K_t}{2} \right)} = \frac{r - 1}{5(r + 1)}.$$

Since r approaches unity in some cases it follows that

$$\frac{\partial \log K_v}{\partial t} = \frac{e'' - e'}{KT^2} = 0.$$

The average energy of the reacting molecules is practically identical with the average energy of the other molecules. This conclusion means that the average molecule has as much chance of being activated by the absorption of energy as the molecules in some special quantum state far removed in energy content from the average. If some molecules are in the low quantum state, unable to absorb the radiation, then preliminary activation may be useful. In such cases

$$\frac{\partial \log K_v}{\partial t} = \frac{e'' - e'}{KT^2} > 0$$

and therefore

$$r = \frac{K_{t+10}}{K_t} > 1.$$

It should be emphasized that in most photochemical reactions the average energy of the reacting molecule is not identical with the average energy of all the other molecules, and hence the temperature coefficients of most of the photochemical reactions are greater than unity.

In the case of bimolecular reactions, in addition to the influence of the term $e'' - e'$ in determining temperature coefficients, it is also necessary to consider the effect of temperature in increasing the number of collisions between the reacting molecules. In gaseous systems the number of collisions will be roughly proportional to the square root of

the absolute temperature, and this will produce a negligible increase in reaction velocity with increasing temperature. In liquid systems the decrease in viscosity with rising temperature may be large enough to produce an appreciable effect on reaction velocity. Since the viscosity of water at room temperature decreases about 20% for a ten degree rise, this might account in some cases, as suggested by Plotnikoff, for the value $r = 1.2$. It should be noted, however, that out of the seven reactions which Plotnikoff classified as belonging to the group with a value 1.2, three are gaseous reactions, so that his explanation can hardly be a general one.

Recently, G. B. Kistiakowsky (*Proc. Nat. Acad. Sci.* **15**, 194 (1929)) has investigated the influence of temperature from 25° to 527° on the photochemical reaction between hydrogen and oxygen, and carbon monoxide and oxygen, from the view point of the thermal reaction chain theory of Semenoff (*Z. Physik.* **48**, 571 (1928)). The results obtained by Kistiakowsky appear to differ widely from the Arrhenius formula (*Z. physik. Chem.* **4**, 226 (1889)), and increase rapidly with rise of temperature; and this is attributed to an increasing quantum yield with rise of temperature. (Compare, Kopp, Kowalsky, Sagulin, and Semenoff (*Z. physik. Chem. B* **6**, 307 (1930)).

Bodenstein, Padelt, and Schumacher (*Z. physik. Chem. B* **5**, 209 (1929)) have studied the temperature coefficient of the thermal reaction between chlorine and ozone, and Lewis, and Schumacher (*Z. Elektrochem.* **35**, 648 (1929)) have obtained 3.05 for the temperature coefficient of the thermal reaction between ozone and bromine. It is concluded that both these changes are chain reactions (compare Alyea and Bäckström (*J. Amer. Chem. Soc.* **51**, 90 (1929)).

The temperature coefficients of thermal reactions in solutions have been reviewed by Rice and co-workers (*J. Amer. Chem. Soc.* **45**, 1401, 1896 (1923)). Recently Rice and Urey (*ibid.* **52**, 95 (1930)) have stated that in solutions a series of unstable complexes of the type postulated by Brönsted (*Z. physik. Chem.* **102**, 169 (1922); *Chemical Review* **5**, 231 (1928)) exist. The energy of activation is the difference between the mean energy of the complexes which react, and the mean energy of all the molecules. (Compare Kassel, *J. Amer. Chem. Soc.* **51**, 1136 (1929).)

CHAPTER XX.

Radiation Hypothesis of Chemical Reactions and Chemical Changes in Infra-red Radiations.

The rapid increase of the velocity of a thermal reaction with increase of temperature is one of the outstanding difficulties in the theoretical treatment of chemical dynamics. With ordinary chemical reactions, which proceed with measurable velocity, the increase in velocity per 10° rise in temperature is usually from 200 to 720 per cent (compare Dhar, *J. Chem. Soc.* **111**, 717 (1917); the reaction between potassium oxalate and iodine, for example, has $K_{35^\circ}/K_{25^\circ} = 7.2$). On kinetic considerations one can account for a 2—3% increase in velocity for a 10° rise in temperature, because the rise in temperature will increase the velocity of the reacting molecules and diminish the viscosity of the medium. For simpler reactions, these influences of the increase of temperature probably tend to increase the rate of collision of the reacting molecules, but for complicated reactions the rate of collision may actually be diminished; there appears to be little hope of explaining the temperature coefficients of chemical reactions purely on the basis of the kinetic theory.

Most of the explanations for the high temperature coefficients of thermal reactions usually centre round the empirical equation of Arrhenius (*Z. physik. Chem.* **4**, 226 (1889)), connecting velocity of reaction and temperature, which may be written

$$\frac{d \log K}{dt} = \frac{Q}{RT^2},$$

where Q is a constant. Arrhenius derived a relation between the variation of an equilibrium constant with temperature and the variation of the reaction velocity with temperature. Consider the equilibrium $B + C \rightleftharpoons A$; we have

$$K = \frac{[A]}{[B] \times [C]},$$

where K is the equilibrium constant and $[A]$, $[B]$, and $[C]$ are the equilibrium concentrations of A , B , and C respectively at the temperature t . The equilibrium constant K will vary with the temperature, and this variation will depend on the heat of the reaction $B + C = A$; the relation is given by the van 't Hoff isochore

$$\frac{d \log K}{dt} = \frac{Q}{RT^2},$$

which in the integrated form is

$$\log \frac{K_1}{K_2} = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where Q is the heat of the reaction.

Considering the hydrolysis of cane sugar by hydrochloric acid in aqueous solution, Arrhenius suggested that the cane sugar is present in two forms, active and inactive, in mass action equilibrium; the equilibrium concentration of the active form is supposed to be very minute and to be attained practically instantaneously; if K is the equilibrium constant of the reaction: active \rightarrow inactive cane sugar molecules, we can evidently write as before

$$K_{35^\circ}/K_{25^\circ} = [A]_{35^\circ}/[A]_{25^\circ}.$$

Arrhenius postulates that only the active molecules undergo hydrolysis, and that the high temperature coefficient of the reaction is due almost wholly to the increase in concentration of the active molecules; $K_{35^\circ}/K_{25^\circ}$ for this reaction is approximately 4, which is also the value for $[A]_{35^\circ}/[A]_{25^\circ}$, so that we can calculate the heat of the reaction: active cane sugar \rightarrow passive cane sugar to be 26,000 cal. per mol. Arrhenius further extended this hypothesis to explain catalysis, by assuming that the hydrogen ion or other catalyst shifts the equilibrium to the active side, and therefore increases the velocity of the reaction.

By applying the considerations of statistical mechanics, Marcelin (*Compt. rend.* **157**, 1419 (1913); **158**, 116, 407 (1914); *Ann. Physique*, (9), **3**, 120 (1915)) and Rice (*Brit. Ass. Rep.* 1915, p. 387) arrived at a relation which is the same as that of Arrhenius. They assume that E in the following equations corresponds to the energy necessary to convert 1 mol of normal molecules into the active state:

$$\frac{d \log K_2}{dT} = \frac{E_2}{RT^2} \quad \text{and} \quad \frac{d \log K_1}{dT} = \frac{E_1}{RT^2} \quad (1)$$

where $E_2 - E_1 = Q$, the heat of the reaction, and $K_2/K_1 = K$, the equilibrium constant. According to Boltzmann's distribution law, the fraction f , of the molecules which will be in the activated state (that is, possess an energy content which exceeds that of normal molecules by E cal. per mol) at temperature T is given by $f = e^{-(E/RT)}$. Hence

$$\frac{d \log f}{dT} = \frac{E}{RT^2};$$

and since the velocity is proportional to f , equation (1) follows as a necessary consequence. According to this theory, therefore, E_2 and E_1 in equation (1) denote the heats of activation for the molecules taking part in the corresponding reactions, and the total energy change (which is the thermally measured heat of reaction) is the difference between the activating or "critical" energies.

It is obvious that the foregoing relations offer no explanation as to the actual mechanism by which molecules become activated. However, Trautz (*Z. wiss. Photochem.* **4**, 160 (1906); *Z. physik. Chem.* **76**, 129 (1911); *Z. anorg. Chem.* **102**, 81 (1918); **106**, 149 (1919)) and subsequently J. Perrin (*Ann. Physique* (9), **11**, 5—108 (1919)) and W. C. McC. Lewis (*J. Chem. Soc.* **109**, 796 (1916); **111**, 387, 457, 1086 (1917); *Phil. Mag.* **39**, 26 (1920)) have advanced the hypothesis that possibly the infra-red radiation, which is necessarily present throughout any system in virtue of its temperature, may be the active agency in promoting chemical change of the ordinary or thermal type, such changes including not only the so-called uncatalyzed reaction, but catalyzed reactions as well, in so far at least as these are met with in homogeneous systems.

Lewis states: "Briefly the hypothesis is, that the increase in internal energy which a molecule must receive before it is capable of reacting (that is, the critical increment E) is communicated to it by infra-red radiant energy present in the system, the addition of energy being made in terms of quanta of the absorbed type".

The principal argument in favour of the radiation theory, or radio-chemical theory, is the existence of unimolecular reactions in a gaseous medium. Perrin in his book "Les Atomes", published in 1913, first referred to the difficulty or impossibility of accounting for the velocity of unimolecular reactions on the basis of the activation of molecules by collisions. The observed rate of a bimolecular reaction is determined only by the rate of collision of activated molecules, since it is assumed that the primary process of activation is very rapid. On the other hand,

the rate of a unimolecular reaction is determined by the rate of interaction of the molecules and the radiation, since collisions can play no part in the reaction. For example, let us consider the decomposition of PH_3 . According to the law of mass action, the velocity of this reaction in an unit volume is proportional to the concentration of PH_3 . In other words, for a definite mass the quantity of the gas decomposed in an unit of time is independent of its volume. If the volume occupied by a definite weight of PH_3 is increased to 10 times its original value, the PH_3 decomposes 10 times less frequently per unit of volume, and consequently the decomposition will be the same in the total mass which now occupies ten times as much space. Thus, although the distances between the molecules have been increased, and the number of collisions is ten times fewer, the duration of life of the PH_3 molecules is not changed.

Perrin has concluded that dissociation is not produced by collisions, and hence he was led to find out the cause of dissociation in the isothermal radiation, which fills the space in which the reacting molecules are being constantly exposed. Later, on generalising and making his ideas more precise, Perrin stated: "Chemical reactions are provoked by radiation; the velocity of a reaction is determined by the intensity of that radiation, and depends only on the temperature in the measure that the intensity depends upon it."

Thus the radiation theory represents an extension of Einstein's law of photochemical equivalence to thermal reactions. In accordance, therefore, with this hypothesis, the chemical action depends upon the absorption of a nearly monochromatic radiation of frequency ν given by the relation $E_c = Nh\nu$, where E_c denotes the critical increment or energy necessary to activate one mol. Furthermore, it follows that the increase in velocity of the reaction with temperature must be due to the increase in radiation density $u_\nu d\nu$ of this radiation, and therefore the temperature coefficient of the velocity constant should be the same as that of the energy density $u_\nu d\nu$. The range $d\nu$ would correspond, according to this point of view, to a narrow region of the spectrum which is absorbed by the molecules taking part in the reaction.

Substituting for $u_\nu d\nu$ the relation derived by Planck, it follows that the velocity of a reaction is given by a relation of the form

$$K = c \times \frac{8\pi\nu^2 h\nu}{e^{h\nu/RT} - 1} d\nu,$$

where c is a constant.

Replacing Planck's relation by Wien's, it is evident that the velocity constant may be expressed as a function of the temperature by the relation:

$$K = K_0 e^{-h\nu/RT} = K_0 e^{-Nh\nu/RT} \quad \text{and} \quad \frac{d \log K}{dT} = \frac{Nh\nu}{RT^2}$$

where K_0 corresponds to the limiting value of the velocity constant at infinitely higher temperatures. Also if ν_1 corresponds to the activating frequency for the reaction in one direction, and ν_2 to the activating frequency for the inverse reaction, then

$$Q = E_2 - E_1 = Nh(\nu_2 - \nu_1) \quad (2)$$

and

$$\frac{d \log K}{dT} = \frac{Nh(\nu_2 - \nu_1)}{RT^2}.$$

In accordance with this theory it would be expected that the frequency ν calculated from the temperature coefficient of the velocity constant should be the same as that absorbed by the reacting molecules, or at least that there should be an absorption band which includes the radiation of frequency ν .

For the purpose of calculating this frequency it is convenient to write the above equation in the form

$$\nu = \frac{E_c}{Nh} = \frac{E_c \times 4.184 \times 10^7}{6.062 \times 10^{23} \times 6.55 \times 10^{-27}} = 1.048 \times 10^{10} E_c,$$

where E_c is expressed in calories per gram-molecule and can be calculated from the temperature coefficient of reaction velocity. It is worth noting in this connection that the equation (2) had been previously deduced by F. Haber (*Ber. deutsch. Physik. Ges.* **13**, 1117 (1911)), and applied by him to the formation of some halide salts from their elements. However, from the above considerations it is evident that equation (2) follows logically from Einstein's law of photo-chemical equivalence, if we assume that similar considerations are valid for thermal reactions.

For reactions which take place at the ordinary temperature with measurable velocity, the temperature coefficients lie generally between 2 and 7, and the active radiations for such reactions belong to a short infra-red region, as will be shown in the following table:

Reaction	Temperature coefficient of the dark velocity	Wavelength Å
(1) Decomposition of $\text{Na}_2\text{Co}(\text{NO}_2)_6$	3.5	13,000
(2) Acetone and I_2 and HCl	3.21	13,800
(3) Rochelle salt and Br_2	3.2	13,800
(4) Potassium oxalate and I_2	7.2	8,600
(5) Potassium oxalate and Br_2	5.6	9,400
(6) Sodium formate and I_2	4.3	10,900
(7) Sodium formate and HgCl_2	4.36	10,800
(8) FeSO_4 and I_2	2.92	14,600
(9) Citric acid and chromic acid and MnSO_4	3.73	12,000
(10) Chromic acid and oxalic acid and MnSO_4	2.94	14,400

The decomposition of PH_3 ought to be activated by radiations of wavelength 3800 Å.

Perrin immediately recognised that a verification of the theory would require the following tests:—(1) the presence of an absorption band in the absorption spectrum of the reacting system of the calculated frequency, (2) the acceleration of the reaction by radiation of the calculated frequency.

The first direct proof that a substance which is undergoing change exhibits a characteristic absorption band, the position of which is in quantitative agreement with that calculated on the radiation hypothesis, was obtained by Taylor and Lewis (*J. Chem. Soc.* **121**, 665 (1922)). The reaction studied was the decomposition of triethyl sulphonium bromide in various solvents; the kinetics of this reaction had been previously studied by von Halban (*Z. physik. Chem.* **67**, 129 (1909)). A Hilger infra-red spectrometer and a radio micrometer as measuring instrument were used. The absorption spectra of the pure solvent, and of a solution of the triethyl sulphonium bromide in the solvent, were examined and superimposed. It was found that the curve for the solution exhibited in every case a new band, which was not present in the solvent curve. This new band was due to the bromide present, and the position was found to agree satisfactorily with that calculated according to the theory. The following table (p. 329) shows the values obtained.

The agreement between the calculated and observed positions of the absorption band is satisfactory in the case of the first six solvents.

Moran and Lewis (*J. Amer. Chem. Soc.* **44**, 2886 (1922)) observed an absorption band in sucrose solution at 8750 Å, whilst the calculated one according to the temperature coefficient should be at 8150 Å.

Absorption of triethyl sulphonium bromide

Solvent	Observed wavelength	Calculated wavelength
	Å	Å
Nitrobenzene	10,500	10,000
Tetrachlorethane	9,000	9,100
Propyl alcohol	8,900	8,400
Amyl alcohol	8,300	8,500
Benzyl alcohol	8,000	7,800
Acetic acid	9,300	9,700
Acetone	13,000	9,600
Chloroform	10,000	8,500

In this connection it will be interesting to consider the following arguments of Hinshelwood (*Chemical Change in Gaseous Systems*, Oxford, Clarendon Press (1926), p. 114). It seems in general that isolated molecules are slow in undergoing chemical transformation.

Research is being carried out on two lines: first, that of finding an explanation of the rarity of unimolecular reactions, and secondly, that of discovering the mechanism by which molecules become activated in these reactions. Activation appears necessary, since unimolecular reactions have high temperature coefficients.

Let us define the unimolecular reaction as a transformation in which the fraction undergoing change in unit time is independent of the pressure over the ordinary range of pressures, without prejudice to what may happen at extremely low pressures.

New light was thrown on the problem by Perrin, who argued that since the velocity of a unimolecular reaction is independent of the pressure, it should be possible to expand the gas to infinite volume without influencing the number of molecules which undergo transformation in unit time. In some way, therefore, isolated molecules, cut off from all communication of energy by collision, become activated for chemical change. Perrin advanced the view that the cause of reaction was therefore to be sought in the action of radiation upon the molecules. This view lent support to the general radiation theory of chemical change put forward originally in an obscure form by Trautz; and considerably developed by W. C. McC. Lewis.

Lindemann (*Trans. Faraday Soc.* 17, 598 (1922)) minimised the force of Perrin's argument by showing that molecules might actually receive their energy of activation by impact from other molecules, and nevertheless be changed chemically at a velocity which was independent

of the pressure over a large range, though not to the limit of infinite dilution, as Perrin had formulated.

It is only necessary to assume that a certain period of time elapses between the moment when a molecule receives the energy by collision and the moment of chemical change. This assumption appears reasonable for, in virtue of the internal electronic motions, molecules are likely to pass through maxima and minima of stability. Lindemann supposes the molecule to be activated by collision, and to decompose only when it passes through its next minimum of stability. If the average time between the activation and chemical change is large compared with that between two impacts, most of the molecules activated by one collision will lose their energy again by a second collision before they have a chance to react. According to this view the velocity of activation is a very different thing from the velocity of reaction. The state of affairs may be represented as follows: normal

activated molecules
 $\text{molecules} \rightleftharpoons \downarrow \text{products of reaction}$

The processes indicated by the

horizontal arrows take place very rapidly compared with that indicated by the vertical arrow. A stationary state is thus set up, in which a constant fraction of the molecules nearly equal to $e^{-E/RT}$ possesses the energy of activation, and can undergo chemical change if they pass through the phase of minimum stability before their next collision. Only a small fraction is transformed in this way, most of it becomes inactive again by loss of energy. The chemical reaction therefore changes the concentration of active molecules very little. The fraction $e^{-E/RT}$ is independent of pressure, and the number of molecules reacting in unit time is a small constant fraction of this. Thus, the number reacting in unit time is also independent of the pressure, and all the conditions of a unimolecular reaction are realized.

At low pressures, however, the time between two collisions must become comparable with the period elapsing between activation and reaction, so that the removal of molecules by chemical change seriously diminishes the stationary concentration of activated molecules. When the pressure is much reduced there must therefore ultimately come a point where the unimolecular velocity constant falls off. Lindemann's mechanism would account for the independence over large ranges, — and this corresponds to our experimental criterion of unimolecularity. Perrin seeks to extrapolate the experimental observations to infinite dilution, which may not be permissible.

The acceleration of many chemical reactions by light shows that

there is nothing improbable in principle about the hypothesis that molecules are activated by the absorption of ordinary temperature radiation. Only the fact that the amount of radiational energy obtained in a gaseous system is small in comparison with the molecular kinetic energy, except at very low pressures, seems at first sight to render the hypothesis of activation by infra-red radiation superfluous, when Perrin's argument has once been met. Nevertheless, many people are in favour of some form of radiation hypothesis.

Another mechanism has been suggested by Christiansen and Kramers (*Z. physik. Chem.* **104**, 451 (1923)) in which activation is assumed to take place by collision, and yet there is an apparently unimolecular reaction. It depends on the view that the products of reaction, possessing the energy corresponding to the heat of reaction as well as the original heat of activation, are able immediately to activate fresh molecules of the reactant. In this way "reaction-chains" are set up. The assumption is made that every molecule of the product can at once activate a fresh molecule of the reactant by collision. In this way each activated molecule removed from the system by chemical change is replaced by a new activated molecule.

The supply of activated molecules is thus maintained (1) by the Maxwell distribution, according to which a constant fraction of the total number is in the active state when there is no removal by chemical change, and (2) by the total replacement of all such removals in the way postulated. The number of active molecules is thus always a constant fraction of the total concentration of reactant, and the change is thus kinetically unimolecular.

We must briefly examine the consequences of the simple radiation theory of unimolecular reactions. The only unimolecular reactions to which it would be necessary to apply this theory would be those in which the value of the velocity coefficient showed no diminution as the concentration was indefinitely decreased. This does not mean to say, however, that activation by absorption of radiation may not be a very general mechanism.

In the activation of molecules a narrow band of infra-red frequency was supposed to be operative. All matter at constant temperature is in equilibrium with radiant energy, which is being continually absorbed and re-emitted in quanta, by the molecules. A space entirely surrounded by material walls of sufficient thickness to be impenetrable to radiation is traversed in all directions by waves of every possible frequency. Unit volume contains a definite amount of radiant energy — the radiation density — determined only by the temperature of the

walls, and distributed among the various frequencies in accordance with Planck's law.

It should be stated that the theory does not stand the test of the presence or absence of an absorption band in the proper region. When matters are complicated by assuming that a complex spectrum of frequencies is operative, the problem tends to evade experimental investigation. According to Daniels and Johnston (*J. Amer. Chem. Soc.* **43**, 53 (1921)) the velocity of decomposition of gaseous nitrogen pentoxide should be accelerated by radiations of wavelength 11,600 Å, a value which is obtained by calculation from the temperature coefficient of the thermal reaction. Exposure of a cell containing nitrogen pentoxide to strong sunlight filtered through iodine solution, which is transparent to wavelength 11,600 Å but opaque to visible light, produced no detectable acceleration of the reaction.

Consequently several authors have declared that the radiation hypothesis fails in two ways — first, because of the inadequacy of the amount of radiation in an isothermal system to provide the energy of activation at the required velocity, and secondly, because experiments on the acceleration of reactions by irradiation with the appropriate infra-red radiation lead to negative results. An investigation of this kind is that of G. N. Lewis and J. E. Mayer (*Proc. Nat. Acad. Sci.* **13**, 8, 623 (1927)); compare Mayer (*J. Amer. Chem. Soc.* **49**, 3033 (1927)), the reaction studied being the racemization of pinene in the gaseous state. The pinene was passed at low pressure through a vessel intensely irradiated with infra-red radiation. The result was that none of the racemization which would have been expected from the theory took place. Very recently Urey and Tolman (*J. Amer. Chem. Soc.* **51**, 974 (1929)) have critically examined the above investigation of Lewis and Mayer, and have concluded that their experiments have not proved the ineffectiveness of radiation up to 13,000 Å in the thermal racemization of pinene, because in their experiments the molecules of pinene were exposed to infra-red radiation only for a short time.

Hibben (*Proc. Nat. Acad. Sci.* **13**, 626 (1927); *J. Amer. Chem. Soc.* **50**, 937, 940 (1928)) has stated that no change in reaction velocity could be detected in the decomposition of nitrous oxide exposed to infra-red radiations at different temperatures, and with different frequencies. The decomposition of ozone at 0° is also uninfluenced by infra-red radiations.

Fromageot (*Bull. Soc. Chem.* (iv) **41**, 1585 (1927)) has shown that the reduction of ceric salts by acetaldehyde in acid solution is not influenced by infra-red radiation; nor does the frequency of the absorbed

radiation, calculated from the temperature coefficient of the reaction velocity, appear to correspond with any of the absorption bands of the aldehyde.

Recently, Kassel (*J. Amer. Chem. Soc.* **51**, 54 (1929)) has reported that radiation of wavelength less than 5μ is not able to increase the decomposition velocity of gaseous nitrogen pentoxide even at low pressures. The view point that thermal unimolecular reactions are to be considered as photochemical reactions, with the activating frequencies lying in the infra-red region, should be susceptible of experimental test, by subjecting a system to radiation from an outside source and determining whether or not the thermal reaction rate is thereby increased. The difficulties of such an experiment arise from two sources. First, there is the necessity of obtaining a high intensity of infra-red radiation. In the second place, the extreme opacity of almost all substances to all but the shortest of infra-red rays makes it difficult to find a window that will permit a high intensity over the wide range of frequencies which may be important in activating the molecules.

Daniels (*J. Amer. Chem. Soc.* **48**, 617 (1927)) has shown that over a considerable range of frequencies the unimolecular velocity of decomposition of N_2O_5 is not appreciably affected by radiation, although Daniels (*ibid.* **47**, 2856 (1925)) states that N_2O_5 has strong absorption bands in the region beyond 30,000 Å.

Recently Urey and Tolman (*J. Amer. Chem. Soc.* **51**, 974 (1929)) have investigated the effect of infra-red radiation on the velocity of racemization of d-pinene in the liquid state. This reaction has been shown by Smith (*J. Amer. Chem. Soc.* **49**, 43 (1927)) to be unimolecular in the gas phase, in the liquid, and in solutions of various organic solvents. The results obtained by Urey and Tolman show that infra-red radiation of wavelength 30,000 Å does not accelerate the rate of racemization of pinene, although according to Coblenz (*Investigations of Infra-red spectra, Carnegie Institution Publication* Number 65 (1907), Vol. III, p. 49) pinene shows strong absorption in the region beyond 30,000 Å.

On the other hand, recently, R. Audubert (*Compt. rend.* **184**, 881 (1927)) has studied the photochemical oxidation of ferrous salts, and the reduction of ferric salts in presence of the same radiations, but with different intensities. From his results he supports the radiochemical theory of Perrin and Lewis.

It was believed that, in visible light, ozone was stable. Recent investigations by Griffith and Shutt (*J. Chem. Soc.* **119**, 1948 (1921)), initiated as a result of calculations made by Lewis (*Trans. Faraday Soc.* **17**, 579 (1922)) in 1918 on the basis of the radiation theory of

chemical action, have shown that ozone may be decomposed by visible light of wavelength longer than 6700 \AA , and therefore in the red region of the visible spectrum. This prediction of Lewis, and its subsequent verification by Griffith and Shutt, is a definite achievement of the radiation hypothesis.

For a certain number of reactions, where the primary effect of light is a dissociation of the molecule into atoms, it has been assumed that the active quantum is equal to the heat of dissociation, and this conception has been applied in the cases of HBr and HI . In a similar way A. Job and Emschwiller (*Compt. rend.* **179**, 52, 168 (1924)) have attempted to determine the energy of the linking C—I in compounds such as $\text{C}_2\text{H}_5\text{I}$, on the supposition that the primary phenomenon produced by light is the dissociation of $\text{C}_2\text{H}_5\text{I}$ into C_2H_5 and I . The hypothesis that the smallest active quantum is equal to the energy of dissociation has been verified by experiments, and has been doubted specially by Franck and Bowen. According to the experiments of Coehn and Jung (*Z. physik. Chem.* **105**, 356 (1923)), the limit of active rays for the formation of HCl from a moist mixture of hydrogen and chlorine is 5400 \AA , which corresponds with the heat of dissociation of chlorine molecules (54,000 calories); but the measurements of Weigert (*Z. physik. Chem.* **120**, 215 (1926)) bring the limit up to 5900 \AA . Similarly, Taylor and collaborators (*Trans. Faraday Soc.* **23**, 31, 38 (1927)) have shown that the active frequencies for the photochemical combination of chlorine and hydrogen are not confined to any restricted regions, since when light is filtered through chlorine, its photochemical effect falls rapidly not towards zero but to a definite residual value. Thus, some of the very feebly absorbed radiations of longer wavelengths must be active in the photochemical combination of chlorine and hydrogen. Bowen (*Z. physik. Chem.* **120**, 157 (1926)) has stated that the value (69,000 calories) found by Job and Emschwiller is not in accordance with the value (40,000 calories) obtained from thermochemical data. It is probable, however, that the dissociation of $\text{C}_2\text{H}_5\text{I}$ is a complex phenomenon, and iodine acts as a photosensitizer for the reaction (compare Stobbe and Schmitt, *Z. wiss. Phot.* **20**, 57 (1920)).

In order to establish a precise relation between the limit of the active wavelength and other constants characteristic of the photo-sensitive substance, it is necessary to know exactly the changes brought about in the molecule for its dissociation or its reaction with other molecules. We have at present a very vague notion on this subject, but it is probable that studies on the absorption spectra of vapours are likely to throw light on the subject. The important researches of V. Henri and

his students (*Structure des molécules*, Paris, 1925) seems promising. Teves (*Thèse*, Zurich (1926)), working under V. Henri, has studied the ultra-violet absorption of sulphur vapour. The absorption of radiations of wavelengths longer than 2794.2 \AA , by molecules of S_2 , leads to a slight disturbance of the atomic nuclei of which the distance is between 0.70 to 0.73 \AA . In the molecules thus modified, all the movements vary by quanta, and this leads to the formation of a fine structure of absorption spectra consisting of numerous lines. When the wavelengths of the absorbed radiations become less than 2794.2 \AA , the fine structure disappears, and the lines are replaced by narrow bands. The velocity of rotational movement does not change suddenly, but continuously. On the other hand, the distance between the atomic nuclei undergoes a sudden increment which causes a weakening of their attraction, and an increase of the chemical activity. Rideal and Norrish (*J. Chem. Soc.* **125**, 2070 (1925)) have stated in their researches on the combination between hydrogen and sulphur that the limit of the active radiation is about 2800 \AA . V. Henri has given the name pre-dissociation to this state of molecules not in the dissociated condition, but chemically active. When the wavelength becomes 2592 \AA , corresponding to $110,000$ calories per gram molecule and a potential of 4.77 volts ($h\nu = Ve$), a new change is produced in the spectra, which still consist of bands. According to Foote and Mohler, 4.77 volts is the resonance potential of sulphur, and is a measure of the energy which renders a molecule fluorescent. The radiations of wavelengths smaller than 2592 \AA make a valency electron pass to a higher orbit. The distance between the atomic nuclei (rings) undergoes an increment. The ionization potential is much higher (12.2 volts), which corresponds to 1005 \AA . Thus, according to the wavelength of the rays absorbed, the sulphur molecule takes 3 different states: 1st, a normal state ($\lambda > 2794.2 \text{ \AA}$) in which all the movements are quantified; 2nd, a state of pre-dissociation ($\lambda < 2794.2 \text{ \AA}$) or chemical activity in which the movements are no longer quantified; 3rd, a state of resonance ($\lambda < 2592 \text{ \AA}$), equally active, in which a valency electron has been transported to a higher orbit. It is needless to emphasize the importance of these observations, which furnish precise information regarding the changes produced in the molecule by light, and these changes render the molecule chemically active.

Recently Dhar and co-workers (*Z. anorg. u. allg. Chem.* **175**, 357 (1928); **176**, 372 (1928); *J. Indian Chem. Soc.* **6**, 451 (1928)) have investigated the kinetics, temperature coefficients, and quantum yields of several chemical reactions under the influence of radiation of mean

wavelength 7304 Å and 8500 Å (light filtered through a deep blue cobalt glass cell containing saturated solution of potassium dichromate), which lie in the infra-red region. Their results show that more than forty chemical reactions are appreciably accelerated by radiations of 7304 Å and 8500 Å. They have carefully measured the extinction coefficient of the reacting substances by Nutting's spectrophotometer, and have found appreciable absorption in the region $\lambda = 7000$ Å. The amount of energy absorbed in the region 8500 Å was determined by Boys' radiomicrometer. It is apparent, therefore, that the reacting substances actually absorb the radiation of wavelengths 7304 Å and 8500 Å, and are activated by the absorption of energy, and then react chemically.

Some years ago Lindemann (*Trans. Faraday Soc.* **17**, 598 (1922)) stated that the hydrolysis of cane sugar is not accelerated by sunlight, although according to the radiation theory it should have been accelerated. This lack of increase of velocity of cane sugar hydrolysis on illumination was advanced as an argument against the radiation theory.

Bhattacharya and Dhar have recently investigated the velocity of cane sugar hydrolysis in radiations of wavelengths 4725 Å, 5650 Å and 7304 Å. All these radiations accelerate the velocity of cane sugar hydrolysis and are actually absorbed by sugar solution as shown by measurements with Nutting's photospectrometer and Boys' radiomicrometer. The quantum yield and temperature coefficients have also been determined in presence of these radiations. These experimental results proved that the statement of Lindemann, that the velocity of sugar inversion is not accelerated by visible radiations, is not correct.

The extinction coefficient of neocyanin shows that the radiations of wavelengths longer than 5670 Å are completely absorbed, even by very dilute solutions of neocyanin. As the wavelength of the incident radiation is decreased, the absorption passes through a minimum, and then increases with the decrease of wavelength. The velocity of the bleaching of neocyanin is greatest in the region $\lambda = 7304$ Å, less in the region $\lambda = 5650$ Å, and least in the region $\lambda = 4725$ Å. This shows that the velocity of reaction and absorption go hand in hand.

Dhar and coworkers have measured photographically the absorption of several of these reacting mixtures, using a Hilger quartz spectrograph with a copper arc as a source of light. With an exposure of about 2 minutes, no absorption was observed with mixtures of chromic acid and organic acids in the region of wavelengths greater than $\lambda = 4275$ Å using a panchromatic plate, but their experimental results on the velo-

city measurements show that these reactions are not only accelerated by radiations of wavelength 4725 \AA and 5650 \AA , which lie in the visible part of the spectrum, but even by radiations of $\lambda = 7304 \text{ \AA}$ and 8500 \AA , which lie in the infra-red region. It appears, therefore, that small amounts of absorption of incident light cannot be observed by a photographic method on short exposure. On the other hand, the extinction coefficient measurements show that all radiations from 7000 \AA to 4400 \AA are actually absorbed by aqueous solutions of neocyanin and a mixture of citric and chromic acids. Similar results, showing appreciable absorption of all radiations from 7000 \AA to 4400 \AA , have been observed with the other reacting systems.

It is well known that the absorption of radiation by molecules is a very complex phenomenon. A very thin layer of mercury vapour shows marked absorption of wavelength 2537 \AA , whilst columns of air 9.5 and 39.4 metres long respectively show feeble absorption of radiations $\lambda = 7600 \text{ \AA}$ and 6900 \AA . These absorptions are ascribed to the oxygen of the atmosphere (compare Foote and Mohler, *Origin of Spectra*, p. 89, (1922); A. S. King, *Astrophys. J.* **55**, 411 (1922)).

The few exceptions to Stokes' law of fluorescence, where the frequency of the emitted light is greater than the frequency of the incident radiation, observed by R. W. Wood (*Phil. Mag.* vii **6**, 310 (1928)) and others with vapours of sodium, iodine, and other fluorescent substances, have been explained from the following point of view: In a system there are a few molecules the energy of which is much greater than the energy of the average molecules. When the incident radiation falls on such an active molecule, the molecule is further activated by the absorption of incident radiation, and under favourable conditions it can revert directly to the inactive state, giving out radiation of greater energy content than that available from the incident radiation. Recently, C. V. Raman (*Indian J. Physics.* **2**, 399 (1928)) has observed this phenomenon (antistokes' effect) with substances such as carbon tetrachloride and benzene, when illuminated by radiation of wavelength 4304 \AA , which is not supposed to be absorbed, but scattered by molecules of CCl_4 or C_6H_6 . It is apparent, therefore, that there can be activating of molecules and a shift towards the shorter wavelength side even with so-called scattered radiations. Incidentally it should be mentioned that this phenomenon of shift of wavelength is a measure of the number of active molecules present in a system.

According to the radiation hypothesis we can easily calculate from the temperature coefficient of the thermal reaction the wavelength of the radiation which should accelerate the chemical reaction. It is

evident from the Table on page 328 that all the reactions should be accelerated by short infra-red radiation. As a matter of fact, Dhar and collaborators have observed accelerations in all reactions studied by them by radiation of wavelength 7304 Å and 8500 Å. They are of the opinion that the wavelengths obtained by calculation from the thermal temperature coefficients may be regarded as the threshold limit. No acceleration of the change is possible with radiations of longer wavelengths than the threshold limit. This point may also be made clear from another line of argument. Following Arrhenius, we know that there are active and inactive molecules in a system, and that chemical changes take place between the active molecules only and it has also been held that an increase in temperature means an increase in the number of active molecules. Now those dark reactions which are very sensitive to the influence of temperature, are evidently the ones where the difference in energy between the active and inactive molecules is very marked. In other words, in activating the inactive molecules in such a system, absorption of energy in quanta of greater energy content would be necessary than in a system where the difference in energy levels between the active and inactive molecules is not so prominent. Dhar (*J.Chem. Soc.* **111**, 707 (1917)) and others have shown that fast dark reactions have smaller temperature coefficients than comparatively slow ones. This is because, in a fast reaction the number of active molecules is much greater than in the slower ones. Hence a fast reaction would not be so sensitive to the influence of temperature. Thus it appears that those reactions which have small temperature coefficients in the dark could be activated by quanta of smaller energy content, and consequently that such reactions should be accelerated by short infra-red radiations. On the other hand, those thermal reactions which are very sensitive to the influence of temperature should be activated by radiations of larger energy quanta, and hence ought to be sensitive to shorter wavelengths.

It must be pointed out clearly that, according to the views advanced by Dhar and co-workers, we can get the threshold frequencies from the measurements of temperature coefficients of the dark reactions. Radiations of longer wavelengths will not promote the reaction in question. The main difference between this conception and the Perrin-Lewis radiation hypothesis is that according to the latter view the wavelength calculated from the temperature coefficient should bring about the maximum speed of the reaction in question, whilst according to the conception now put forward by Dhar, the threshold frequency is the minimum frequency necessary for the carrying out of the reaction.

The foregoing conclusion is corroborated by the observation of W. Taylor and collaborators (*Trans. Farad. Soc.* **23**, 31, 38 (1927)), that the active frequencies for the photochemical combination of hydrogen and chlorine are not confined to any restricted regions, since when light is filtered through chlorine, its photochemical effect falls rapidly not towards zero but towards a definite residual value. Thus, some of the very feebly absorbed frequency must be active in the photochemical combination of hydrogen and chlorine. From the foregoing experimental results and conclusions it will be clear that the main argument raised by Langmuir (*J. Amer. Chem. Soc.* **42**, 2090 (1920)), Lindemann (*Trans. Faraday Soc.* **17**, 598 (1922)), Polányi (*Z. Physik.* **1**, 337; **2**, 90 (1920)), and others against the radiation hypothesis of chemical change, that reacting substances do not show absorption of such radiations as are obtained from the temperature coefficients of thermal reactions, loses its force.

It should be emphasized that the heats of dissociation of molecules of chlorine, bromine, and iodine are as follows: 54,000 cal. (Cl_2), 45,200 cal. (Br_2) and 35,200 cal. (I_2). Now the corresponding wavelengths, which can be obtained by calculation from these heats of dissociation, and which are capable of atomizing the molecules of the halogens, have the following values: 5400 Å (Cl_2), 6230 Å (Br_2), and 8360 Å (I_2). Our experimental results show that radiations of wavelengths 7304 Å and 8500 Å can accelerate numerous photochemical reactions involving the halogens. Consequently these wavelengths accelerate the photochemical changes involving chlorine, bromine, and iodine, not by the production of atoms of halogens but possibly by the formation of active halogen molecules by absorption of these radiations.

CHAPTER XXI.

Influence of Light Intensity on the Velocity of Photochemical Reactions.

We (Bhattacharya and Dhar, *Z. anorg. Chem.* **169**, 381 (1928); **175**, 357 (1928); *J. Indian Chem. Soc.* **6**, 197, 493 (1929); *J. Chim. phys.* **26**, 556 (1929)); Verma and Dhar (*Z. anorg. Chem.* **184**, 90 (1929); Mukerji and Dhar (*J. Phys. Chem.* **32**, 1308 (1928); *Z. Elektrochem.* **32**, 501 (1928)) have investigated the influence of the variation of intensity of the incident radiation on the velocity of more than 40 photochemical reactions. By changing the diameter of the aperture of an iris diaphragm, the amount of light falling on the reaction vessel and hence the intensity were varied. In all the reactions, the velocities in the dark were deducted from the total change observed in light in order to get the velocity in light alone.

The source of light in most reactions was a 1000 Watt gas-filled tungsten filament lamp, operated at 4.6 amperes. In some reactions, sunlight was also utilized, whilst in others light-filters were used. The reactions investigated under the above conditions in these laboratories may be classified in the three following groups:

(1) Velocity tends to be proportional to the square of the incident radiation.

(2) Velocity tends to be directly proportional to the intensity.

(3) Velocity tends to be proportional to the square root of the intensity.

Our experimental results show that the velocities of the majority of the reactions are proportional to the square root of the incident radiation. Hence we have concluded that the velocities of really photochemical reactions are proportional to the square root of the intensity of the incident radiation. We have advanced the view that the two important factors, which are of consequence in the relation between intensity and the velocity of a reaction are: (a) The amount of absorption of the incident radiation by the reacting system. (b) The acceleration of the reaction in presence of light. When the absorption of radiation is high, the reaction is not markedly photochemical in

nature, and the velocity of the reaction in the dark is appreciable, direct proportionality or even square of intensity is likely to be observed. On the other hand, when the reaction is highly photochemical in nature and the velocity of the dark reaction is practically negligible, square root or less than square root relationship will be expected. It will be evident, therefore, from the foregoing lines that if a reaction, which is proportional to the square of the intensity of the incident radiation, can be greatly accelerated by the incidence of strong light, it should show a tendency to follow the direct or square root relationship. On the other hand, a reaction following the square root relationship can be made to be proportional directly to the intensity, if the dark velocity of such a reaction can be greatly accelerated, and the reacting system is exposed to radiation which is not intense and is slightly absorbed by that system (compare Allmand, *J. Chem. Soc.* 1557 (1929)).

We have been successful in changing the relationship between the intensity and the velocity, by changing the velocity of the dark reaction, and the intensity and quality of the incident radiation in the following reactions: (1) potassium oxalate and iodine, (2) rochelle salt and bromine, (3) quinine sulphate and chromic acid, (4) sodium formate and iodine, (5) potassium nitrite and iodine, (6) hydrazine hydrochloride and iodine, (7) hydroxylamine hydrochloride, and iodine, (8) oxalic acid and chlorine in presence of hydrochloric acid, and several other reactions.

Berthoud and Bellenot (*Helv. Chim. Acta* **7**, 307 (1924)), and Briers, Chapman, and Walters (*J. Chem. Soc.* **129**, 562 (1926)) have found that the reaction between potassium oxalate and iodine is proportional to the square root of the light intensity. Mukerji and Dhar (*J. Phys. Chem.* **32**, 1308 (1928)) have observed that the reactions between potassium oxalate and iodine, and ammonium oxalate and iodine are proportional to the square root of the incident radiation. The reaction between potassium oxalate, and iodine (dissolved in potassium iodide) which is proportional to the square root of the intensity of radiation (from a 1000 Watt gas-filled tungsten filament lamp and of light of wavelength 4725 Å) tends to be directly proportional to the intensity of radiation of wavelengths 5650, 7304, and 8500 Å in absence of potassium iodide. We have observed that these radiations are only slightly absorbed by the reacting system.

Similarly, the reactions between rochelle salt and bromine, quinine sulphate and chromic acid, sodium formate and iodine, and several other reactions, can show square root, direct, or nearly square relation-

ship depending on the acceleration caused by light. Hence, it appears that by increasing the velocity of the dark reaction, and exposing it to radiation which is slightly absorbed by the reacting system, a truly photochemical reaction, which is proportional to the square root of the incident radiation or the amount of energy absorbed, becomes directly proportional to the intensity of the incident radiation or the amount of energy absorbed. On the other hand, a photochemical reaction which is proportional to the square of the incident radiation, or is directly proportional, can be made to be proportional to the square root of the incident radiation by decreasing the dark reaction velocity and increasing the photochemical velocity. Our experimental results and conclusions throw a flood of light on the highly controversial question of the relation between intensity and velocity in the reaction between chlorine and hydrogen (compare Bhattacharya and Dhar, *J. Chim. phys.* **26**, 556 (1929)).

In order to make sure that the absorption of radiation is proportional to the intensity of the incident radiation, we have determined the absorption of the incident radiation by a radiomicrometer. We have observed that the amount of radiation absorbed is directly proportional to the intensity of the incident radiation.

Other workers have used different methods for altering the light intensity. Interposition of a number of sheets of tissue paper of known extinction, of various forms of diaphragms of known fractional aperture or of crossed Nicol prisms; change in slit width when working with dispersed monochromatic light; variation of distance between light source and reaction vessel; and a rotating sector have been utilized.

Direct proportionality between intensity and velocity has been found in the cases of hydrolysis of chloroplatinic acids (Boll, *Ann. Phys.* (IX) **2**, 5, 226 (1914)), the decompositions of solutions of hydrogen peroxide, potassium cobaltioxalate (Vránek, *Z. Elektrochem.* **23**, 336 (1917)), and potassium manganioxalate (Ghosh and Kappanna, *J. Indian Chem. Soc.* **3**, 127 (1926), and for the initial photolysis of uranyl formate solutions (Hatt, *Z. physik. Chem.* **92**, 513 (1918)). Moreover, we have shown that a solution of dicyanin can be decolorized by passing oxygen in the dark, and the influence of light intensity on the photochemical bleaching of dicyanin shows direct proportionality. Now in all these cases, there is an appreciable dark reaction, and in presence of light the velocity of the reaction is not enormously increased.

On the other hand, Warburg and Negelein (*Z. physik. Chem.* **106** 191 (1923)) found that in the carbon dioxide assimilation process sensi-

tized by chlorophyll, the rate of assimilation increases less rapidly than the intensity. It is well known that no combination of carbon dioxide and moisture takes place in the dark even in presence of chlorophyll, and hence carbon assimilation is a typically photochemical reaction, where the velocity does not increase proportionately with the intensity of light. According to Berthoud (*Trans. Faraday Soc.* **21**, 554 (1925); *Helv. Chim. Acta.* **10**, 475 (1927)), the square root relation holds for addition of bromine to cinnamic acid, to α -phenyl cinnamionitrile, and to stilbene and the oxidation of HI in presence of iodine. In all these cases the reactions are highly accelerated by light, and the reaction velocity in the dark is very small in comparison with the photochemical velocity. Bodenstein and Lütkemeyer (*Z. physik. Chem.* **114**, 208 (1924)) have announced that the union of hydrogen and bromine in light is proportional to the square root of the energy absorbed when the intensity of light is kept constant. It will be interesting to observe that the velocity of the same reaction taking place in light is 300 times as great as that taking place in the dark. Consequently the combination of bromine and hydrogen is highly photochemical in nature. Briers and Chapman (*J. Chem. Soc.* 1807 (1928)) have recently found that the rate of interaction of hydrogen and bromine for very high intensity of light approximates to values which have a square root relation to the values of the intensity, but for low intensities the rate becomes more nearly equal to values proportional to intensity. These results of Briers and Chapman have recently been confirmed by Bodenstein, Jost, and Jung (*J. Chem. Soc.* 1153 (1929)). Those reactions where square root or less than square root relationship is observed, are largely accelerated by light, and their thermal reaction velocities are extremely small in comparison with the reaction in light alone. In these reactions many molecules are readily activated by the absorption of radiation on illumination, and consequently further increase in light intensity is not likely to increase the reaction markedly (compare Wegscheider, *Monatsh.* **51**, 285 (1929), and Allmand (*J. Chem. Soc.* 1557 (1929)).

A fast dark reaction, when illuminated, has much less chance of showing direct proportionality relationship than a slow reaction, because in a fast reaction many more molecules are in the active state, and there is less chance of further activation of molecules on increased illumination than in the case of slow reactions. As a matter of fact, our experimental results show that the reactions between potassium permanganate and lactic acid, tartaric acid, or citric acid, in presence of strong light, increase much less rapidly than intensity, and these reactions have been proved to be fast in the dark.

The majority of researchers in photochemistry have assumed that the amount of chemical change in a given system effected by light of a specified wavelength is directly proportional to the light absorbed. Following the lead of Draper, this has been called the first law of photochemistry. Although this is a fundamental principle of greatest importance, the experimental evidence of its universal validity is not conclusive. From a survey of our experimental results obtained with 40 photochemical reactions, and the existing literature in photochemistry, we have come to the conclusion that the amount of chemical change in a truly photochemical system, where the reaction is largely accelerated by light, is proportional to the square root or even less than square root of the absorbed light. We have shown that in the case of several photochemical reactions the relation between velocity and intensity of incident radiation changes from $\frac{1}{4}$ to 2. In other words, we have definitely shown that the ratio of the velocity and intensity of photochemical reactions can vary from a proper fraction to 2 or more, depending on the acceleration of the photochemical reaction over the thermal reaction.

Baly and Barker (*loc. cit.*), and others, have assumed that those reactions which do not obey the Einstein Law of photochemical equivalence should deviate from the Grotthus-Draper Law. We have shown that the bleaching of neocyanin in air follows Einstein's law of photochemical equivalence, but that this reaction is proportional to the square root of the incident radiation. Moreover, the reactions between iodine and tartrate, lactate, citrate, or ferrous sulphate, and in several other cases, the velocities are directly proportional to the intensity of incident radiation and hence follow the Grotthus-Draper law, although they deviate considerably from Einstein's law of photochemical equivalence; in all these reactions many more molecules react per quantum of light absorbed. Hence those reactions which obey Einstein's law need not follow the Grotthus-Draper law and *vice versa*.

In recent years Berthoud (*Helv. Chim. Acta.* **7**, 324 (1924)) has emphasized that the primary process in the photochemical reactions with a halogen as one of the reacting substances, is the dissociation of the halogen molecules into atoms as the result of their absorption of light, the halogen atoms then reacting at a rate proportional to the first power of their concentration. This contention of Berthoud appears to be supported by the fact that several photochemical reactions are nearly proportional to the square root of the incident radiation. We have observed that the reaction between potassium oxalate and iodine is proportional to the square root of the incident radiation from a 1000 Watt gas-filled tungsten filament lamp; whilst the reaction

between sodium lactate and iodine is directly proportional to the intensity. If we assume that in presence of light a molecule of iodine is atomized, we can explain the intensity effect on the reaction between potassium oxalate and iodine; but this conception that the halogens are atomized when illuminated does not help us in understanding the mechanism of those photochemical reactions with halogen as one of the reacting substances, where the velocity of reaction is directly proportional or proportional to the square of the intensity of the incident radiation. Our experimental results show that the reaction between sodium lactate and iodine is only slightly accelerated by light, and consequently the inactive molecules available for activation on illumination are large, and hence direct proportionality is observed. Moreover, we have shown definitely that the ratio of the velocity and intensity of one and the same photochemical reaction can vary from a proper fraction to 2 or more, depending on the acceleration of the photochemical reaction over the thermal reaction. From the foregoing results and conclusions, it will be clear, therefore, that Berthoud's view, that the halogen molecule is atomized on illumination, need not be always correct.

CHAPTER XXII.

Influence of Temperature on Quantum Yield and the Variation of Extinction Coefficient with Increase of Temperature.

The experimental results recorded in Chapters VI to XII show that, in general, the quantum efficiency increases with the increase in the temperature of the reacting substances.

Mukerji, Bhattacharya, and Dhar (*J. Phys. Chem.* **32**, 1834 (1928)) have carried out measurements of the extinction coefficients of some photochemically reacting substances. In every case it has been found that the absorption of radiation markedly increases with increase in temperature.

The increase in extinction coefficients, that is, the amount of absorption of light with increase of temperature, can be explained from the point of view of the change of hydration of the solutes at higher temperature. The amount of hydration of a solute is likely to decrease on increase of temperature, and this frequently leads to changes in the absorption. As the solvates become simpler on increase of temperature, the absorption of light is likely to increase. It is generally found that the effect of increasing the temperature of the solution is the same as that of increasing the concentration of the solute. In both the cases there is a widening of the absorption bands — that is, the absorption of light increases owing to the solvates becoming simpler (compare H. C. Jones, *The Nature of Solutions*, page 331 (1916)). Consequently, the increased quantum yield on increase of temperature of the reacting substances appears to be associated with the increase in the light absorption on increase of temperature. It is interesting to note that in various photochemical reactions, the ratio of the quantum yields at different temperatures is greater, the greater the temperature coefficient of the reaction.

INFLUENCE OF WAVELENGTH ON QUANTUM YIELD.

From the experimental results (Chapters V to XIII) it will be seen that in most cases the quantum efficiency at different temperatures

increases with the frequency of the incident radiation. This is probably due to the fact that the total energy of the absorbed quantum goes on increasing with the frequency of the incident radiation. In other words, the power of a quantum of light energy to induce a photochemical change is greater, the greater the frequency of the incident radiation.

According to the law of photochemical equivalence, one molecule should decompose per quantum of energy absorbed, independently of the frequency of the incident energy. This requirement of the law is well fulfilled in the cases of the decomposition of gaseous hydrogen bromide and hydrogen iodide, and less accurately in the case of the decomposition of solid AgBr, and in the transformation of o-nitrobenzaldehyde to o-nitrosobenzoic acid.

Henri and Wurmser, and also Lasareff, have obtained an approximate proportionality between the photochemical effect and the amount of light of different wavelengths absorbed. The experiments of Lasareff have been carried out with the velocity of decolorization of the following substances impregnated in collodion: pinaverdol, lepidincyanine, cyanine, pinachrom, quinaldin-cyanine, and pinacyanol. Thin layers of collodion impregnated with these substances and placed on glass plates, were exposed to light of different wavelengths. The quantity of radiant energy absorbed was measured bolometrically or spectrometrically, and the velocity of decolorization determined by an optical method. For most of the substances studied by Lasareff, a parallelism between the photochemical effect and the amount of light absorbed was observed. From his results, Lasareff concluded that the photochemical effect for the same quantity of the light absorbed is the same for all the rays belonging to the photochemical absorption band. This view is in disagreement with the equivalence law, and appears to be unwarranted from the results of Lasareff, who did not obtain exact proportionality between the amount of radiant energy absorbed and the matter transformed. Thus in the case of cyanin, the ratio between the amount of radiant energy absorbed and the matter transformed for radiation of wavelengths 6300 Å and 5500 Å differed by 16%. This deviation is expected from the Einstein Law. In the decomposition of hydrogen peroxide solution by short wavelengths (Tian, *Ann. Physique* **8**, IX, 226 (1916)), and in the transformation of maleic ester to fumaric ester when sensitized by bromine (Eggert and Borinski, *Z. Physik.* **24**, 504 (1923)), it is observed that a definite amount of energy causes the same amount of chemical change, whatever the wavelength of light. The variations of the quantum yield have been attributed to different causes. It is possible that the duration of the active state, and con-

sequently the probability of the molecule entering into reaction, goes on increasing with the increase in the value of the quantum absorbed. It seems probable that an active molecule loses its energy in several phases, and in small quanta. If it has absorbed radiations of large frequency, it possesses more energy than is necessary for its activation, and consequently it conserves its faculty of chemical transformation after having lost a part of this energy. Hence the active state of such a molecule is likely to be longer than that of another molecule which has absorbed a quantum which is of smaller energy content than the previous one, and is only just sufficient for activation.

Recently, Henri and Wurmser (*J. Phys. Radium* (VI), **8**, 289 (1927)) have stated that the photochemical reaction as a whole does not obey Einstein's law of photochemical equivalence, but in general, the primary process of such a reaction, consisting of activation, pre-dissociation, or dissociation of the molecule, does so. The study of the fluorescence, the absorption spectra, and other conditions for a reaction in the gaseous state, makes it possible to decide in which of these three ways the elementary process takes place. In other cases, the quantum efficiency of a photochemical reaction increases with the frequency of the light used, owing to the different modes of activation produced by radiations of increasing frequency.

It has been already emphasized that in exothermal reactions there is a natural tendency for the photochemical yield to be greater than that required by Einstein's law. It is interesting to note that the quantum yields of these reactions increase markedly with the increase in frequency of the radiation used.

INFLUENCE OF INTENSITY ON QUANTUM YIELD.

The following experimental results (p. 349) have been obtained regarding the influence of intensity on quantum yield.

Similar decrease of quantum yield with increase of light intensity has been observed with several other photochemical reactions.

The results (p. 349) show that the quantum yield decreases as the amount of light falling on the reacting substance is increased. Using a radiomicrometer we have measured the amount of light absorbed by these reacting substances, and we have observed that this is directly proportional to the amount of the incident radiation. Similar results have been obtained with 30 photochemical reactions investigated by us. Hence we can conclude that in these reactions, which show high quantum yields, the intensity of the incident radiation influences the quantum yield, and that the greater the light intensity

the less is the quantum yield. (Compare Winther, *Z. physik. Chem.* 120, 32 (1926)).

No.	Source of light	Reaction mixture	Temp. ° C	Diameter of the aperture of the iris diaphragm. cms.	Quantum yield
1	1000Watt lamp	20% cane sugar (15 c.c.) and N/20 HCl (5 c.c.)	35	2 0.8	16.5×10^2 19.2×10^2
2	4725 Å	N/101.7 bromine and 43% methyl alcohol (10 c.c. each)	20	2 0.8	6.2 7.9
3	4725 Å	N/113.7 bromine and 25% ethyl alcohol (10 c.c. each)	20	2 0.8	3.2 4.6
4	4725 Å	49% acetone (5 c.c.), N/50 iodine (10 c.c.) and N/9.42 HCl (5 c.c.)	31	2 0.8	41 53
5	4725 Å	N/4.72 lactic acid (5 c.c.) and N/86.2 KMnO ₄ (10 c.c.) in presence of N/69.5 MnSO ₄ (5 c.c.)	29	2 0.8	71 83
6	4725 Å	N/5.36 tartaric acid (5 c.c.) and N/98.45K MnO ₄ (10 c.c.) in presence of N/69 MnSO ₄ (5 c.c.)	36	2 0.8	93 132
7	4725 Å	N/4.69 sodium lactate and N/100 iodine (10 c.c. each)	30	2 0.8	14 22
8	4725 Å	N/2.42 sodium tartrate and N/100 iodine (10 c.c. each)	30	2 0.8	15 19
9	4725 Å	6.75 N citric acid and N/44.4 chromic acid (10 c.c. each)	34	2 0.8	8 11.6
10	4725 Å	N/4.27 tartaric acid and N/44.4 chromic acid (10 c.c. each)	32	2 0.8	14.6 18.6

CHAPTER XXIII.

Chemiluminescence.

It is well known that in the decomposition of ozone, ammonium bichromate, potassium permanganate, etc. considerable heat is generated. In other words, the decomposition of ozone takes place according to the following equation: $2\text{O}_3 \rightarrow 3\text{O}_2 + \text{Energy}$. Now in these cases, the energy of the chemical change is mostly converted into infrared radiations, but under certain conditions the decomposition of ozone is associated with the giving out of a part of the energy of the chemical change as visible radiation. Similarly, a part of the energy of the decomposition of ammonium dichromate comes out as visible radiation. On the other hand, the thermal decomposition of potassium permanganate is not associated with the emission of the energy as visible radiation. The giving out of energy in a chemical change as visible radiation, is known as chemiluminescence. No definite relation has been obtained as yet between the amount of energy to be given out as light energy and as heat energy. Moreover, we do not know as yet which type of chemical changes are likely to give out light. Apart from the well known case of the glow of phosphorus, in recent years numerous cases of chemiluminescence have been investigated. Thus chemiluminescence has been observed in the slow oxidation of magnesium alkyl halides (Lifschitz and Kalberer, *Z. physik. Chem.* **102**, 393 (1922); Dufford and co-workers, *J. Amer. Chem. Soc.* **45**, 2058 (1923); **47**, 95 (1925)), organic sulphur compounds (Délepine, *Compt. rend.* **174**, 1291 (1922)), and several silicon compounds (Kautsky and Zocher, *Z. Physik.* **9**, 267 (1922), *Faraday Soc. Discussion*, (October 1925)). Kautsky and co-workers (*Z. Elektrochem.* **29**, 308 (1923); *Z. Physik.* **9**, 302, 267 (1922); **31**, 1 (1923); *Z. anorg. Chem.* **117**, 209 (1921); **139**, 135 (1924); **141**, 1 (1925); **147**, 81 (1925); *Trans. Farad. Soc.* **21**, 591 (1925)) showed that the oxidation of silicone at room temperature leads to a bright chemiluminescence. Silicone is a yellow solid substance, a mixture of siloxane ($\text{Si}_2\text{O}_3\text{H}_6$) and several coloured reaction products of siloxane. Most of these solid silicon derivatives (e.g. silico-oxalic acid, siloxane, etc.) are colourless, and are built up of lamellæ consisting of layers one or two molecules thick, which lie over one another like

leaves of a book. These substances form coloured adsorption compounds with basic dyestuffs (rhodamine, rhodamine sulphonate, etc.) and these fluoresce. The lamellæ can be oxidized by adding small quantities of potassium permanganate in acid solution, without showing chemiluminescence, and without change in their morphological structure. The chemiluminescence which is caused by adding a solution of permanganate to these adsorption compounds is surprisingly bright. The same chemiluminescence is observed if the adsorption compounds in the dry state are oxidized with ozone. This is due, as is assumed by Kautsky, to the fact that the adsorbed dye causes the chemiluminescence. Kautsky showed that the spectral distribution of this induced chemiluminescence is identical with the usual fluorescence spectrum of the same dyestuff, and the emission of light is due not to a partial oxidation of the dyestuff by potassium permanganate but to the oxidation of siloxen. It is concluded that the reaction energy is transmitted from the reaction products to molecules of the dye, and the resulting excitation is identical with that produced by the dye on absorption of radiant energy. The energy must evidently be transmitted by some sort of collision between the adsorbed dyestuff and the neighbouring reacting siloxen molecules.

Moreover, Kautsky and Thiele (*Z. anorg. Chem.* **144**, 197 (1925)) observed that whereas siloxen reacts rapidly with inorganic chlorine compounds, chlorine substituted organic substances do not react with siloxen in the dark. On illumination, however, reaction takes place between siloxen and chlorine substituted organic compounds, and the chemical change seems to be autocatalytic. Kautsky and Thiele demonstrated that the autocatalysis is due to intermediate coloured halogen derivatives, which photosensitize the reaction of siloxen in light. A similar photosensitization to visible light has already been discussed with rhodamine and rhodamine sulphonate, but the dyestuff must be adsorbed for this type of sensitization.

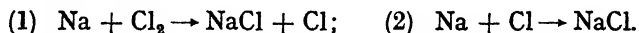
The chemiluminescence observed in the oxidation of siloxen containing rhodamine and rhodamine sulphonate by potassium permanganate appears to be the opposite of the sensitization observed in the photochemical reaction of siloxen with the organic chlorine derivatives with the intermediate coloured halogen derivatives.

CHEMILUMINESCENCE BY COMBINATION OF ATOMIC HYDROGEN AND OTHER REACTIONS.

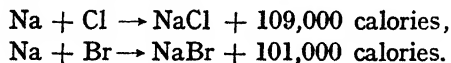
(Bonhoeffer (*Z. physik. Chem.* **116**, 394 (1925)) observed that when hydrogen atoms recombine in presence of alkali metal vapours or

anthracene, a chemiluminescence is excited, and the emitted spectrum is the same as the line spectrum of the metal vapour or the ordinary fluorescence spectrum of anthracene. Only those lines were observed by Bonhoeffer, of which the quantum energy is less than the heat of recombination of hydrogen atoms, except for the fact that the mercury line 2536 Å is emitted when liquid mercury is present in the system. The excitation of the mercury line 2536 Å requires 112,000 calories, whereas the recombination of hydrogen atoms can supply 101,000 calories. In order to explain this discrepancy, Bonhoeffer pointed out that along with the mercury line 2536 Å, certain bands which are supposed by Compton and Turner (*Phil. Mag* **48**, 360 (1924)) to be due to HgH are emitted, showing that the mechanism of excitation of mercury atoms involves several steps in which the necessary quantum energy is gradually accumulated. Kaplan (*Nature* **126**, 48 (1927)) has shown that a blue glow, the spectrum of which extends from 5000 to 4400 Å, is obtained by having an incandescent tungsten filament in wet hydrogen at 20–350 mm. pressure.

Recently other cases of induced chemiluminescence have been studied. Haber and Zisch (*Z. Physik.* **9**, 302 (1922)) observed that vaporised metals react with halogens with emission of light. With alkali metal vapours the light consisted mainly of the resonance lines—the D lines of sodium or the corresponding lines of other alkali metals; with mercury the resonance line 2536 Å was not emitted. The explanation was suggested that the heat of reaction of mercury with hydrogen is insufficient for the excitation of mercury atoms. Kallmann and Franz (*Naturwiss.* **13**, 441 (1925)) showed, however, that the mercury line 2536 Å is emitted when a mixture of sodium and mercury reacts with chlorine, but not with bromine. Kallmann and Franz suggested that the reactions of metals with halogens proceeded in two steps:



The products of the second reaction are likely to possess a large plus energy, which is equal to:

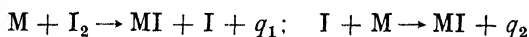


It seems, therefore, that mercury atoms, requiring 112,000 calories for excitation, may be activated more readily on collision with a newly formed NaCl molecule than with a NaBr molecule.

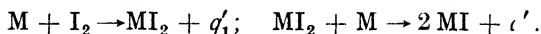
Moreover, Polányi and Beutler (*Naturwiss.* **13**, 441 (1925)) showed that, not only the reaction of sodium vapour with free halogen

accompanied by emission of the D lines, but also its reaction with different mercury halides and other inorganic halides, but not with organic halogen derivatives. Polányi and Beutler state that the reaction between sodium and iodine proceeds in two steps, and that the first step, which is not accompanied by chemiluminescence, takes place on every collision of the reacting substances; the second reaction is about 100 times slower than the first at a pressure of about 0.01 mm., but is accompanied by emission of the line spectrum of the alkali metal. They estimated the intensity of the emitted light, and came to the conclusion that about 10^{-4} of all collisions of sodium and iodine atoms are followed by the emission of light.

On the other hand, Ljalikov and Terenin (*Z. Physik.* **40**, 107 (1926)) studied spectroscopically the reaction between different alkali metals and iodine, and pointed out that besides the reaction mechanism already mentioned:



with heats of reaction q_1 and q_2 , the whole process is assumed to take place in the following steps:



These authors suggest that the reactions of alkali metal with iodine proceed according to the second scheme, and that the heat of reaction q'_2 is divided equally between the two MI molecules formed. According to the quantum theory, no line in the emission spectrum could be observed, the quantum energy of which ($Nh\nu$) is larger than that (q) of the reaction.

In the following tables the results obtained by Ljalikov and Terenin are recorded, and the observed lines are denoted by an asterisk:

Metal + I ₂	q_1 Cal.	q_2 Cal.	$\frac{1}{2} q'_2$ Cal.	Terms of the lines	λ	$Nh\nu$ Cal.
Li	64,000	98,000	81,000	1S—2 P	6708*	42,000*
				1S—3 P	3233	88,000
Na	48,000	82,000	65,000	1S—2 P	5890.6*	48,000*
				1S—3 P	3302.3	86,000
K	54,000	88,000	71,000	1S—2 P	7666*	37,000*
				1S—3 P	4044.8*	70,000*
Rb	54,000	88,000	71,000	1S—4 P	3446.7	82,000
				1S—2 P	7800.9*	37,000*
				1S—3 P	4202.1*	67,000*
				1S—4 P	3349.5	85,000

These experimental results are in agreement with the mechanism suggested by Ljalikov and Terenin, since no line with quantum energy higher than $\frac{1}{2}q'_2$ has been obtained.

Beutler, Bogdandy and Polányi (*Naturwiss.* **14**, 164 (1926)) investigated the reactions of sodium vapour with other halogens, and showed that in some cases spectral lines of quantum energy higher than q_2 were emitted. Ljalikov and Terenin explained this discrepancy from the view point of an unequal distribution of the reaction energy q'_2 between the molecules formed, or the formation of an intermediate compound M_2Cl_2 with double energy content. Beutler and Polányi (*Z. Physik.* **47**, 379 (1928)) have suggested that the light emission in these cases is from the secondary reaction $Na_2 + Cl \rightarrow NaCl + Na$, in which the NaCl molecule retains the reaction energy, and by collision transmits this energy to a free sodium atom. The reaction $Na + Cl$ proceeds at a thousandth of the speed of the reaction $Na_2 + Cl \rightarrow NaCl + Na$. The primary reaction between sodium and chlorine is $Na + Cl_2 \rightarrow NaCl + Cl$ and is nonluminescent. Polányi and Schay (*Z. Physik.* **47**, 814 (1928)) have shown that highly attenuated flames of alkali metals burning in stannic chloride, bromide, and iodide emit intense luminescence and continuous bands. The bands extend from 4000 to 5500 Å with potassium and stannic chloride, from 4050 to 5400 Å with sodium and stannic chloride, from 4400 to 6000 Å with sodium and stannic bromide, and from 5000 to 6200 Å with sodium and stannic iodide. The intensity is greatest in the middle of the band, and decreases symmetrically on each side. The chemiluminescence is explained by supposing a trihalide to be first formed, and that this decomposes into the di- and tetrahalides with evolution of light.

Moreover, Polányi and Schay (*Z. physik. Chem. B.* **1**, 30, 62, 68 (1928)) and Bogdandy and Polányi (*ibid.*, 21 (1928)) have suggested that the following reactions take place in the chemiluminescence observed in the interaction of sodium vapour and halogens or mercuric chloride: (1) In the alkali metal vapour and halogen, the primary reaction is $Na + Cl_2 \rightarrow NaCl + Cl$, followed by the reaction $Na_2 + Cl \rightarrow NaCl + Na$, taking place on the walls of the tube, and the reaction $Na_2 + Cl \rightarrow NaCl + Na$, which produces light in the gaseous phase. (2) In the alkali metal vapour and mercury chloride, the primary reaction is $Na + HgCl_2 \rightarrow NaCl + HgCl$, and the secondary one $Na + HgCl = NaCl + Na$.

The "true light emission", which gives the probability of the sodium chloride molecule formed by the elementary process $Na + Cl_2 \rightarrow NaCl + Cl$ emits light by collision with a sodium atom

this indicates that a considerable portion of the chemical energy is transformed into vibrational energy. The velocity coefficient for the reaction $\text{Na}_2 + \text{Cl} = \text{NaCl} + \text{Na}$, when $c = 0.7$, is calculated to be 4×10^{-7} .

When iodine is substituted for chlorine, the "true light emission" of the elementary process $\text{Na}_2 + \text{I} = \text{NaI} + \text{Na}$ in sodium vapour is about 0.4. The velocity coefficient of this reaction is 5×10^{-8} .

For the sodium-mercuric chloride flame, the velocity coefficient of the primary reaction $\text{Na} + \text{HgCl}_2 = \text{NaCl} + \text{HgCl}$ is approximately 1.5×10^{-6} , and for the secondary reaction $\text{Na} + \text{HgCl} = \text{NaCl} + \text{Hg}$, it is 1×10^{-7} .

Very recently, Frommer and Polányi (*Z. physik. Chem. B*, **6**, 371 (1930)) have studied the chemiluminescence observed in the heterogeneous reactions between metals and chlorine. In the case of aluminium, the intermediate formation of AlCl_2 , and with copper, CuCl , has been assumed.

Bonhoeffer and Harteck (*Z. physik. Chem.* **139**, 64 (1928)) have shown that when hydrocarbon vapours, except methane, are allowed to mix with a stream of monatomic hydrogen, a greenish blue light, resembling that of the inner cone of the Bunsen flame, is emitted. The results show that monatomic hydrogen may hydrogenate and dehydrogenate hydrocarbons, and may rupture very stable rings.

Kondratjew (*Nature* **121**, 671 (1928)) has suggested that the exciter of chemiluminescence in the reaction between alkali atoms and halogens is a molecule NaCl^* , having an excess of energy, and existing as an energy-rich molecule for a sufficiently long time to meet a sodium atom. Kondratjew (*Z. Physik.* **48**, 310 (1928)) has studied the reaction between sodium and potassium vapour and the vapour of cupric chloride and bromide, in the neighbourhood of 300° . The spectrum of the light emitted by the reacting vapour is that of the corresponding cuprous halide. Following a discussion of the energy changes taking place with the formation of excited molecules of the cuprous halide, it is concluded that the reaction takes place at the surface of the containing vessel between solid cupric halide and gaseous alkali metal, forming gaseous cuprous halide and solid alkali metal halide. On the other hand, the reaction between sodium and mercuric chloride vapours appears to be homogeneous.

Moreover, Kondratjew and Leipunski (*Naturwiss.* **16**, 463 (1928); *Z. Physik.* **50**, 366 (1928)) have examined the light emitted by heating iodine to 1000° in air, and in a vacuum. Bands are observed in the

red, yellow, and green regions. It is concluded that the light has its origin in the reunion of an excited iodine atom with a normal atom to form a molecule. In the cases of other halogens similar results are obtained (compare also articles in the *Bull. Nat. Res. Council U. S. A.* Nos. 7, 23, 30, 41, 59 (1927)).

Recently, Ludlam, Reid, and Soutar (*Proc. Roy. Soc. Edin.* **49**, 156 (1929)) observed that the flame of chlorine burning at a jet in hydrogen consists of a livid white portion surrounded by a pale blue cone. When hydrogen burns in chlorine, however, this pale blue cone almost disappears owing to the extensive absorption of chlorine in the violet. The maximum intensity of the continuous spectrum from the white inner portion occurs in the green. It is suggested that the reaction between hydrogen and chlorine proceeds through two stages, (a) $\text{H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H}$; (b) $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$. The existence of the white flame is ascribed to the combination of free chlorine atoms.

It appears, therefore, from the foregoing discussion, that the activation energy of a light emitting atom can be transmitted to it on collision with energy-rich reacting molecules, and that the relation between the wavelengths emitted by the heat of the reaction is given by the quantum laws. Moreover, the mechanism of induced chemiluminescence appears to be the reversal of the phenomenon of photosensitization, but all photosensitized reactions cannot be accounted for by a simple scheme involving only a transfer of energy on collisions of the primarily excited atoms or molecules of sensitizer with the reacting molecules. In certain cases, an intermediate formation of molecular compounds or of adsorption complexes appears to be in better agreement with experimental results.

Miss Kearney (*Phil. Mag.* **47**, 48 (1924)) has observed a feeble glow when ozonized oxygen is passed through solutions of aesculin in water, acetone, methyl, ethyl, and propyl alcohols, and the intensity of the glow is in the following order in different solvents:

Solvent	Intensity of glow
Ethyl alcohol	5
Propyl alcohol	5
Methyl alcohol	3
Acetone	3
Distilled water	1
Glycerol	0

Recently, we (Biswas and Dhar, *Z. anorg. Chem.* **173**, 123, 186, 154 (1930)) have investigated the glow observed with dyes and organic substances when oxidized by ozone or

peroxide. When ozonized oxygen is passed through solutions of different fluorescent and non-fluorescent dyes, a glow is observed. In non-aqueous solutions, the glow is more pronounced than in the aqueous solutions. The wavelengths of the light given out by the glow with different dyes are as follows:

Dye	Solvent	Wavelengths of light
Eosin	Methyl alcohol	6020 to 5320 Å
Uranine	Ethyl alcohol	5860 to 5030 Å
Neutral red	Methyl alcohol	6050 to 4850 Å
Rhodamine B	Ethyl alcohol	6170 to 4670 Å
Thioflavine	Ethyl alcohol	5700 to 4690 Å
Carthamine	Methyl alcohol	6650 to 4580 Å
Rhodamine B. J. N. N.	Ethyl alcohol	6190 to 4620 Å
Erythrosin	Ethyl alcohol	6060 to 5310 Å
Carthamine	Ethyl alcohol	6050 to 5680 Å
Rhodamine	Ethyl alcohol	5910 to 5530 Å

The foregoing fluorescent dyes gave out the best glow amongst the numerous dyes investigated by us. When ozonized oxygen is passed through solutions of the following fluorescent and non-fluorescent substances, a glow is also observed, but the intensity of the glow is less than that obtained with the first group of fluorescent dyes: methyl blue, alizarin, resorcinol benzene, azure eosin, rose benzal, theonine, methylene blue 2 B, chlorophyll, resorcinol succinyl, resorcinol acetone dicarboxylene, gallein, fluorescein alkaline, and aesculin. There are several other dyes in which the glow was less marked than in the two previous groups. Recently, we have observed that several dyes, when oxidized by hydrogen peroxide and ferrous sulphate, become luminous. In this case both fluorescent and non-fluorescent dyes when oxidized by hydrogen peroxide and ferrous sulphate give out glow.

Several organic and inorganic reducing agents, and some alkaloids, exert a retarding effect on the production of glow by the action of ozonized oxygen on dyes. For example, hydroquinone, sodium sulphite, nicotine, brucine, cocaine, caffeine, cinnamic aldehyde, turpentine, anisaldehyde, nitrobenzaldehyde, strychnine, cane sugar, grape sugar, etc. markedly check the generation of the glow when ozonized oxygen is passed through solutions of dyes containing them.

It is interesting to note that the glow is intense when the dyes are fluorescent. It seems likely that some molecules of the dyes are directly oxidized on passing ozonized oxygen through their solutions, and this oxidation produces radiations, and possibly ions which would

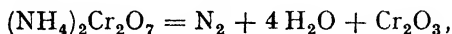
be taken up by the unoxidized molecules of the dye, and thus the molecule would be activated. Some of the active molecules in their turn would react chemically with ozone and oxygen, and would give out radiations. On the other hand, some of the activated molecules without chemically reacting would revert to the normal inactive state, and would give out the extra amount of energy as a glow. It appears that fluorescent substances have the peculiar property of being readily activated by the absorption of radiations and ions. Moreover, the activated molecules of the fluorescent substances have a greater tendency to revert to the normal state, and give out the radiation as a glow, than to react chemically. From the fact that by opening the rings of fluorescent closed chain compounds, and introducing unsaturated groups at the point of fission, compounds which are very sensitive to light are obtained, it has been concluded by Kogel (*Z. wiss. Phot.* **26**, 311 (1929)) that fluorescence is a criterion of photochemical activity. If, however, owing to structural or physical conditions, reaction is not possible, the fluorescence represents only potential activity. The principal groups giving rise to photochemical sensitivity are: $\text{CH}:\text{CH}$., $\text{CH}:\text{N}$., $\text{C}:\text{O}$., .NO_2 ., $\text{.NCl}:\text{N}$, and $\text{N}:\text{N}$. Recently, Ghosh (*Z. physik. Chem. B*, **3**, 419 (1929)), in discussing the mechanism of photochemical changes occurring in a fluorescing electrolyte, has attributed the E.M.F. generated in a cell containing a solution of a fluorescent material, in which there are two platinum electrodes, one of which is illuminated, to the formation of an unstable intermediate product.

The chemiluminescent spectrum of rhodamine B extends from 6170 to 4670 Å, and the fluorescence spectrum, as recorded by Kautsky and Neitzke (*Z. Physik.* **31**, 60 (1925)), consist of lines from 6680 to 4400 Å. Hence it appears that the chemiluminescence spectrum and the fluorescent spectrum of rhodamine B are not altogether identical, as has been assumed by Kautsky (*Trans. Faraday Soc.* (October 1925)). Moreover, it has been shown that there is no theoretical reason why the chemiluminescent and fluorescent spectra should be identical (compare Dhar, *Z. anorg. Chem.* **155**, 303 (1926)).

We have been able to detect a glow in the oxidation of about 20 fluorescent and non-fluorescent substances when oxidized by oxygen, oxygen or hydrogen peroxide, aided by ferrous sulphate; but numerous other coloured substances when oxidized do not give out any glow. In all cases we have observed that the glow is intensified when the solutions are warmed up before oxidation. We have investigated the slow oxidation of numerous substances by passing air, and

not been able to observe a glow. Hence the phenomenon of auto-oxidation is not always accompanied by chemiluminescence. Consequently the view of Jorissen (*Chem. Weekblad* **1**, 789, 817 (1904)), and Moureu and Dufraisse (*Reports of the Solvay International Council of Chemistry, Brussels*, page 524, (April 1925)) that slow oxidation is always accompanied by a light phenomenon seems to be too general.

Most of these oxidation reactions are highly exothermal chemical changes, so that they give out large amounts of energy when oxidation takes place, and in many cases a part of the energy is given out as visible or ultra-violet radiation. In the decomposition of ammonium dichromate according to the equation:



a considerable amount of heat is generated, and a glow is also observed. The decomposition of solid potassium permanganate is also a highly exothermic reaction, but no glow is detected in this change. When small bits of metallic sodium are rubbed in a mortar with solid mercuric chloride, bromide, or iodide small explosions with glow take place. When powdered antimony is dropped into chlorine gas, a glow is also observed. The oxidation of phosphorus, the decomposition of ozone, and the foregoing chemical changes already mentioned are highly exothermal reactions, and a part of the energy of the chemical change is absorbed by the original substance, or products of the chemical change, and they would thus be activated. In the reversion of the activated molecules to the inactive state, a glow is given out.

Dhar (*J. Phys. Chem.* **28**, 948 (1924); *Z. anorg. Chem.* **141**, 1 (1924); **144**, 307 (1924); **159**, 103 (1926)) has emphasized the fact that electron emission in exothermal chemical reactions is of common occurrence. Richardson and Brotherton (*Proc. Roy. Soc., A* **115**, 20 (1927)) have shown that the energy of the electrons emitted in the reaction between carbonyl chloride and a liquid alloy of Na and K corresponds to a temperature of about 3300°. The radiation at this temperature will certainly contain wavelengths shorter than 2537 Å, and possibly will extend up to 2000 Å. Hence, if a little mercury is added to the reacting mixture of carbonyl chloride and liquid alloy of Na and K, the mercury line 2537 Å, will also be excited. Haber and Zisch (*Z. Physik.* **9**, 302 (1922)) have shown that in the reaction between Na and Cl, D-lines are given out corresponding to an energy excitation of 48,300 calories, and the heat of the reaction is 70,000 calories. Fränz and Kallmann (*Z. Physik.* **34**, 924 (1925)) have shown that in presence of mercury, the line 2537 Å corresponding to 110,000 calories is excited. This

peculiar behaviour has not yet been satisfactorily explained. We have suggested the following explanation: when sodium and chlorine react, electrons are generated, and the energy of the electrons corresponds to a temperature of about 2400° . Now the radiations corresponding to this temperature would contain lines of wavelengths 2537 \AA , possibly of feeble intensity. Hence the electrons given out in the reaction of sodium and chlorine containing this amount of energy will be absorbed by the mercury atoms, which would be activated corresponding to a temperature of about 2400° , and when these activated molecules reverted to the inactive state, radiations of wavelength 2537 \AA would be generated. In this connection it will be interesting to note that Garner and Blench (*J. Chem. Soc.* **125**, 1288 (1925)) have obtained 60,000 calories at low temperature, and 220,000 calories at high temperature, as the heat of adsorption of oxygen in charcoal. It seems likely that this adsorption is really a highly exothermal chemical change, which would give out radiations of short wavelengths, and these would be absorbed by the reacting substances which would be activated. A similar explanation seems plausible in the activation of hydrogen on platinum and palladium surfaces. Recently Finch and Stimson (*Proc. Roy. Soc. A* **116**, 379 (1927)) have shown that a gold or silver surface becomes electrically charged when heated in contact with a gas. It seems probable that the surfaces are chemically reacted upon by the gas, and that electron emission takes place in this chemical change. These results are in support of the view that the activation of gases like hydrogen and oxygen at solid surfaces is caused by the taking up of the ions and electrons given out by the adsorption of the gases on the solid surfaces, and that these adsorption processes are mostly chemical changes.

It has been suggested (Dhar, *Z. anorg. Chem.* **159**, 103 (1926)) that in presence of moisture, a complex, containing the reacting substances, moisture, and the ions generated as the product of the chemical change, is formed. The mobility of this complex is less than that of the reacting substances. Hence in presence of moisture, the tendency for activation of reacting substances by the absorption of the ions generated is increased, because of the greater time of contact of the reacting substances with the ions. Hence in presence of moisture, chemical changes are accelerated.

Recently, Lord Rayleigh (*Proc. Roy. Soc. A* **99**, 372 (1922), **104**, 322 (1923)) in studying the chemiluminescence of phosphorus, has come to the conclusion that the glow must be attributed to the

vision of nuclei and that the process is to some extent analogous to the crystallization of a supersaturated solution, the inhibitors are supposed to act by taking prior possession of the nuclei, and thus making them incapable for propagation of the glow. We think, however, that in presence of moisture, a complex, containing the reacting substances and ions generated in the change, is formed. If this complex can be destroyed, either by drying the reacting substances or by the removal of oxygen with turpentine, ethylene, etc. which are good reducing agents, the reactions can be retarded.

We have observed that the intensity of the glow given out in the oxidation of dyes becomes less with the increase in the concentration of the dyes. Perrin (*Compt. rend.* **177**, 612, 665, 714 (1923)) and others have shown that the intensity of fluorescence decreases considerably as the solution is concentrated.

Perrin (*Ann. d. Phys.* (9) **10**, 133 (1918); *Compt. rend.* **178**, 1401 (1924)) advanced the view that the phenomenon of fluorescence is due to the decomposition of molecules of the fluorescent substances. In other words, Perrin included fluorescence in the domain of chemiluminescence. Wood (*Phil. Mag.* (6) **43**, 757 (1922)) supported the hypothesis of Perrin, from his experiments on rhodamin. Weigert (*Z. Physik.* **10**, 349 (1922)), Pringsheim (*ibid.* **10**, 176 (1922)), McLennan and Miss Cale (*Proc. Roy. Soc.* **102 A**, 256 (1922)), Miss Kearney (*Phil. Mag.* **47**, 48 (1924)), and Chakravarti and Dhar (*Z. anorg. Chem.* **142**, 299 (1925)) showed that the bleaching of fluorescent substances is not caused by fluorescence, but is due to the oxidation of the organic compounds by oxygen of air. Chakravarti and Dhar have shown that dye solutions are unstable chemical compounds, and are readily reduced or oxidized, and that these solutions when exposed to visible light are oxidized by the dissolved oxygen, and hence that there is bleaching on exposure to light. In presence of strong light, especially ultra-violet radiations, some of these dyes are actually decomposed, just as solutions of ammonium nitrite, potassium persulphate, trichloroacetic acid, etc. are decomposed by light. Hence the bleaching of dyes on exposure to light is in most cases due to oxidation, and in some cases, when the illumination is very intense, due to decomposition, and has nothing to do with the fluorescence of the substances. Hence the phenomenon of fluorescence cannot be included in the category of chemiluminescence.

In recent years, the chemiluminescence in the oxidation of phosphorus is being extensively investigated by numerous workers, but it is not clear what actually happens during the oxidation of phosphorus.

We shall briefly discuss some of the salient features of this chemiluminescence. It is very peculiar that phosphorus will not glow in oxygen at ordinary atmospheric pressure and temperature, but if the oxygen is rarefied the glow at once begins, and stops immediately the oxygen is compressed. If the glow were simply an oxidation process, the converse should have been true. It appears that the oxidation of phosphorus take place in two steps — the first stage involves the oxidation of phosphorus to the trioxide, with practically no glow, and the second stage the oxidation of the trioxide to the pentoxide with glow. It seems very probable that the luminosity is produced by the oxidation of the vapour of phosphorus. Phosphorus is slightly volatile at the ordinary temperature, and the increased volatilization which occurs when the pressure of the gas is diminished appears to account for the increased luminescence in a rarefied atmosphere.

The glow of phosphorous oxide presents features similar to those in the glow of phosphorus itself. Consequently, it has been inferred that the glow of phosphorus is due to the phosphorous oxide formed in the preliminary non-luminous oxidation.

Petrikaln (*Z. Physik.* **22**, 119 (1924)) has found that in the ultra-violet spectrum of glowing phosphorus, maxima occur at 3270, 2600, 2530, 2460 and 2390 Å, in agreement with the bands in the arc spectrum of phosphorus pentoxide. Emeléus and co-workers (*J. Chem. Soc.* **127**, 1362 (1925); **129**, 1336 (1926); 788 (1927)) have reported that the light from burning phosphorus, that from glowing phosphorus, that from glowing phosphorous oxide, and that from phosphine burning in oxygen, give the same spectrum. These observations seem to indicate that there is some radiating system involved in them all, which gives rise to a definite band spectrum.

Downey (*J. Chem. Soc.* **125**, 347, 2491 (1924)) showed that ozone is formed by the action of light given out by the glowing of phosphorus, and the formation of ozone is proportional to the intensity of the glow. The glow of phosphorus trioxide is assumed by Downey to exert similar influence. A. L. Hughes (*Proc. Cambridge Phil. Soc.* **45**, 483 (1910)) reported that the glow of phosphorus gives out radiation in the regions 1200—1800 Å, which are capable of ionizing air, and this is observed in the burning of phosphorus. W. Busse (*Ann. Physik.* **82**, 873 (1927); (4) **83**, 80 (1927)) doubted if rays between 1200—1800 Å are generated at all in the glow of phosphorus, and he and Petrikaln showed that the production of ozone formed during the reaction is not a photochemical effect of the glow.

Dhar (*Z. anorg. Chem.* **159**, 103 (1926)) has advanced the view that the ozone molecules are formed by activation of the molecules of oxygen through the absorption of ions generated in the oxidation of phosphorus, and at least a part of the glow is possibly due to the reversal of the activated molecules of the reacting substances, and the products of the change, to the normal state.

Eder (*Sitzber. Akad. Wien* **112**, 249 (1903)) showed that the actinic properties of the light from burning phosphorus are much less than those of burning magnesium or aluminium.

According to Weiser and Garrison (*J. Phys. Chem.* **25**, 61, 349, 473 (1921)) the chemiluminescence of phosphorus vapour is not altered appreciably by charging the element electrically. Ions are formed during the oxidation of phosphorus trioxide, and render the surrounding atmosphere a conductor.

It is interesting to note that Serono and Cruto (*Gazzetta* **59**, 402 (1928)) have reported that organic phosphatides present in impure cholesterol, after ultra-violet irradiation, possess the property of affecting a photographic film. It is shown that this is due to the re-emission of ultra-violet light by the phosphatides. Similar results are obtained with pure cerebrin and with chlorophyll.

CHAPTER XXIV.

Influence of Solvent on Photochemical Reactions.

It has been assumed that solvents play an important part in those reactions which do not follow the Einstein Law of equivalence, but the question of the influence of solvents on the velocity of photochemical reactions has not been thoroughly studied. The oxidation of iodoform (Plotnikoff, *Z. physik. Chem.* **75**, 396 (1911)), the polymerization of anthracene (Luther and Weigert, *Z. physik. Chem.* **53**, 393 (1905)), and the action of bromine on toluene (Bruner and Czarnecki), have been investigated in different solvents having different dielectric constants. The experimental results are recorded in the following table:

Solvent	Dielectric constant	Velocity of Oxidation of iodoform	Velocity of Poly-merization of anthracene	Velocity of Bromination of toluene
CCl_4	2.25	39.4	—	100
C_6H_6	2.29	34.6	355	320
$\text{C}_6\text{H}_5\text{CH}_3$	2.33	—	163	..
Xylene	2.38	—	52	..
CS_2	2.61	24.1	—	108
$(\text{C}_2\text{H}_5)_2\text{O}$	4.30	17.0
Anisol	4.35	—	18.6	..
Phenetole	4.3	—	18.0	..
$\text{CH}_3\text{COOC}_2\text{H}_5$	6.1	8.1	—	..
CH_3OH	31.2	3.2
$\text{C}_2\text{H}_5\text{OH}$	25.8	2.3
CH_3COCH_3	21.5	0.7
$\text{C}_6\text{H}_5\text{NO}_2$	37.8	10

From the foregoing results, Winther (*Z. physik. Chem.* **120**, 234 (1926)) has concluded that the velocity of a photochemical reaction decreases as the dielectric constant increases. This rule seems to be unexpected, because in thermal reactions the reverse phenomena have been observed. It appears, however, that there are several exceptions to this generalisation of Winther. Thus Euler (*Ber.* **49**, 1366 (1916)) has shown that the photochemical decomposition of halogenated acetic

acid is more rapid in ether with the dielectric constant of 4.3 than in benzene having a dielectric constant of 2.3. Similarly Lifschitz and Joffe (*Z. physik. Chem.* **97**, 426 (1921)) have shown that the photochemical transformation of triphenylmethane derivatives takes place more rapidly in alcohol ($D = 31$) than in benzene or ether. Plotnikoff (*Z. wiss. Phot.* **21**, 117 (1922)) has observed that the photopolymerization of vinyl chloride takes place in alcohol, but not in CS_2 . The photochemical transformation of p-chloroacetanilide has been found by Mathews and Williamson (*J. Amer. Chem. Soc.* **45**, 2574 (1923)) to take place more slowly in benzene ($D = 2.29$) than in acetic acid ($D = 9.7$). The influence of the solvent appears to be due to the changes in absorption ascribed to the formation of molecular complexes with the photosensitive substance and the solvent. Thus, according to Andrich and Le Blanc (*Z. Elektrochem.* **20**, 543 (1914)), the bromination of toluene in ultra-violet light is slower in toluene than in hexane. In ethyl acetate the velocity is practically nil. In hexane the absorption is selective, and the absorption spectrum is very similar to that of pure bromine. In toluene and ethyl acetate, on the contrary, the spectrum is continuous in the ultra-violet, and this is ascribed to the association of molecules of bromine with the solvent. The differences in the velocity of oxidation of ethyl iodide in ethyl alcohol, in carbon tetrachloride, and in benzene, as observed by Stobbe and Schmitt (*Z. wiss. Phot.* **20**, 57 (1920)), are also due to the difference in the light absorption caused by the presence of iodine, which acts as a photosensitizer or as an internal filter. Hence it can be concluded that the influence of the solvent on a photochemical reaction is controlled by several factors, and appears to be more complex than the influence of the solvent on a thermal reaction.

Plotnikoff and Weber (*Z. Elektrochem.* **34**, 316 (1928)) have discussed the partition of light between two media forming a homogeneous mixture.

Mathur, Gupta, and Bhatnagar (*Indian J. Physics.* **2**, 243 (1928)) have investigated the influence of the dielectric constant of the medium on the velocity of photobromination of cinnamic acid in carbon tetrachloride, carbon disulphide, ethyl ether, chloroform, ethyl formate, ethyl bromide, and ethyl acetate. The conversion of o-nitrobenzaldehyde into o-nitrosobenzoic acid has also been investigated in acetone, ether, methyl ethyl ketone, chloroform, and benzene. Contrary to the suggestion of Winther, no direct relationship can be observed between the velocity coefficients and the dielectric constants of the solvents employed.

Recently, Williams (*J. Chem. Soc.* 1383 (1929)) has shown that in the bromination of coumarin, the thermal velocity of the reaction is greater in chloroform than in carbon tetrachloride solution. On the other hand, the photobromination is greater in carbon tetrachloride than in chloroform.

RETARDING ACTION OF OXYGEN.

Oxygen acts in several photochemical reactions as a negative catalyst. Its retarding influence on the photosynthesis of hydrochloric acid has already been described. It also retards the photosynthesis of phosgene gas. Luther and Goldberg (*Z. physik. Chem.* **56**, 43 (1906)) have shown that oxygen is a retarder in all photochlorinations, and they are of the opinion that the effect is due to the absorption by oxygen of the radiation re-emitted by chlorine. Bodenstein and Dux (*ibid.* **85**, 297 (1913)) advance the view that oxygen exerts an inhibiting influence on all secondary photochemical reactions, except those in which oxygen takes part. According to the measurements of Chapman and Gee (*J. Chem. Soc.* **99**, 1726 (1911)), the velocity of the photosynthesis of carbonyl chloride varies inversely as the pressure of oxygen, when this pressure is feeble. When the pressure becomes larger, the product of velocity and the oxygen concentration increases, and finally, when the pressure of oxygen becomes greater than 20% of the gaseous mixture, the photosensitivity becomes constant. The results can be expressed by a relation of the form:

$$v = A + \frac{B}{[O_2]},$$

where A and B are constants. Similarly oxygen has a retarding action in the photochlorination of organic substances, in the Eder reaction (Jodlbauer and Tappeiner, *Ber.* **38**, 2602 (1905)), in the photodecomposition of ferric oxalate (Jodlbauer, *Z. physik. Chem.* **59**, 513 (1907)) as well as in the bromination of toluene.

Winther and Oxholt-Howe (*Z. wiss. Phot.* **14**, 196 (1914)) have stated that oxygen retards the photo-reduction of ferric salts by different organic acids. Dhar (*J. Chem. Soc.* **111**, 707 (1917)) has shown that oxygen retards and carbon dioxide markedly accelerates the reduction of mercuric chloride by potassium oxalate in the dark. Recently Allmand and Webb (*J. Chem. Soc.* 1518 (1929)) have shown that the photolysis of potassium ferric oxalate is markedly retarded by air, and the reaction practically stops on bubbling oxygen through

the solution. On the other hand, Boll and Henri (*Compt. rend.* **158**, 32 (1914)) have stated that the photochemical reaction between uranyl nitrate and oxalic acid is not affected by oxygen. They observed that oxygen takes part in the reaction by oxidizing the uranous compound produced by the photolysis to the uranyl condition. Moreover Weigert (*Nernst-Festschrift* 464 (1912)) has stated that the velocity of oxidation of quinine by oxygen decreases when the pressure of the gas increases. In this reaction the violet and ultra-violet rays are active. In dilute solutions the velocity can be expressed by the relation

$$v = KI_0 \frac{[\text{quinine}]^2}{[\text{O}_2]}.$$

This retarding action, which was also observed by Weigert in the oxidation of erythrosin, is particularly striking, because oxygen takes part in the reaction. It is well known that a similar phenomenon has been observed in the auto-oxidation of phosphorus in the dark, as well as in the oxidation of certain organic matters accompanied by chemiluminescence.

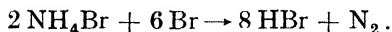
Although oxygen retards the formation of phosgene under the action of light, it appears to have no influence on the thermal reaction. The behaviour of NO is similar to that of oxygen. Now the experiments of Christiansen (*Z. physik. Chem.* **103**, 99 (1923)), and those of Bodenstein and Plaut (*Z. physik. Chem.* **110**, 399 (1924)), have shown that in the thermal reaction the chlorine atoms are active. According to Christiansen, it can be supposed that NO and O₂ retard the photochemical but not the thermal reaction, on the assumption that atomic chlorine is not affected by these substances, which accelerate the de-activation of chlorine molecules which have absorbed a quantum and are in the activated condition.

Recently, Dunnicliff and Joshi (*J. Indian Chem. Soc.* **6**, 121 (1929)) have shown that the oxidation of lactic acid by bromine water and the decomposition of some silver halides are retarded by oxygen.

PHOTOCHEMICAL INDUCTION.

The phenomenon of induction in the photosynthesis of hydrochloric acid has already been considered. This phenomenon has also been observed with several other photochemical and thermal reactions. A photochemical induction in the reaction of chlorine on formaldehyde due to the presence of ammonia has been observed by Burgess and

Chapman (*J. Chem. Soc.* **89**, 1402 (1906)), and by Berthoud and Bellenot (*Helv. Chim. Acta* **7**, 307 (1924)) in the oxidation of potassium oxalate by bromine. The atomic bromine, which is supposed to be formed by the action of light, reacts on NH_4Br according to the reaction:



The destruction of atomic bromine naturally leads to the arrest of the oxidation of oxalate. Moreover, Chapman and Gee (*J. Chem. Soc.* **99**, 1726 (1911)) have observed a period of induction in the formation of phosgene in presence of NH_3 , NCl_3 , or O_3 . The induction period observed in the bromination of toluene has been ascribed by Bruner and collaborators (*Bull. Acad. Sc. Cracow (A)* 516, 520 (1910)) to the presence of oxygen, which acts as a negative catalyst. However, it was not possible to regularize the reaction on eliminating oxygen, but the addition of a small quantity of iodine removed the period of induction. Benrath and Oberbach (*Z. physik. Chem.* **98**, 498 (1921)) have observed a long period of induction in the photochemical decomposition of Fehling's solution. After exposure to sunlight for some time, there is the formation of a deposit of Cu_2O . From this time there is evolution of hydrogen even in the dark. Cu_2O acts in this decomposition as a heterogeneous catalyst. A solution of rochelle salt, which does not give out a gas in light, decomposes immediately if Cu_2O , or metallic copper in the powder form, is added.

A photographic plate is only affected if the quantity of light which falls on it passes a certain limit, below which there is no blackening after the development. This is possibly a phenomenon of induction.

In the action of light on Eder's mixture, the separation of calomel is not immediate, but the photochemical induction is possibly only apparent, because the solution must be saturated with calomel before it can separate out.

Jorissen and Ringer (*Chem. Zentralbl.* **76 I**, 187 (1905)) have shown that there is a period of induction in the photo-oxidation of benzaldehyde. In the oxidation of tartaric acid by bromine, an induction period was observed in light by Bunsen and Roscoe (*Pogg. Ann.* **100**, 513 (1857); *Phil. Trans.* **147**, 355, 601 (1857)), and Ghosh and Mukherjee (*J. Indian Chem. Soc.* **2**, 165 (1925)), and in the dark by Sanyal and Dhar (*Z. anorg. Chem.* **139**, 161 (1924)). Recently Purkayastha (*J. Indian Chem. Soc.* **5**, 721 (1928)) has observed induction periods in the photobrominations of cinnamic acid, and stilbene, and oxidations of mandelic and β -phenyl α -lactic acids by bromine. Potassium bromide diminishes, and in some cases causes the complete disappearance of

the induction period. In all these cases, increase of temperature and of the intensity and frequency of the incident radiation, diminishes the induction period.

✓ Ghosh and Basu (*J. Indian Chem. Soc.* **5**, 361 (1928)) have put forward a suggestion to explain the induction period observed in the oxidation of tartaric acid by bromine. They suggest that in the initial stage of the reaction, the bromine atoms produced by light absorption are used up in destroying the photo-inhibitors, which are almost always present in the reaction mixtures, and consequently the reaction will proceed at a slower rate at the beginning.

Sanyal and Dhar (*Z. anorg. Chem.* **139**, 161 (1924)) have investigated the induction periods of numerous reactions in diffused daylight. It appears that there are, at least, two important causes of the occurrence of the induction period in photochemical reactions: (1) the existence of oxygen, which retards several photochemical reactions; in presence of even small quantities of oxygen, the velocities of the photochemical reactions will be greatly retarded and hence there will be the appearance of induction periods; and (2) the occurrence of chemical reactions in different steps. It is well known that some chemical reactions take place in stages. Thus we have shown that in the reduction of iodic acid by sulphurous or arsenious acid, hypiodous acid is an intermediate product. Similarly, from electric conductivity measurements of different reacting substances, evidence in favour of the existence of intermediate stages has been adduced.

PHOTOCHEMICAL AFTER-EFFECT.

It happens sometimes that a reaction started by light continues in the dark even if the light is cut off. This after-effect is observed in the bromination of toluene, and the decomposition of Fehling's solution. The phenomenon of after-effect has been observed by Szilard (*Z. wiss. Phot.* **4**, 127 (1904)), and later by Plotnikoff (*Z. physik. Chem.* **76**, 743 (1911)), in the oxidation of iodoform by free oxygen in solvents other than alcohol. In alcoholic solution the oxidation of iodoform takes place in light, and the reaction stops as soon as the light is cut off. If CCl_4 , $\text{CH}_3\text{COOC}_2\text{H}_5$, and specially benzene solutions are used, the oxidation continues in the dark with a velocity which is less than in light, and it decreases slowly with the concentration of iodoform.

W. Kistiakowsky (*Z. physik. Chem.* **35**, 431 (1900)) has stated that in presence of $\text{K}_4\text{Fe}(\text{CN})_6$ or $\text{K}_3\text{Fe}(\text{CN})_6$, which acts as photosensitizer,

the photochemical decomposition of H_2O_2 , which takes place in visible light, continues practically at the same velocity even when the light is cut off. Weigert (*Ann. d. Phys.* **24**, 261 (1907)) has observed that the thermal decomposition of H_2O_2 is accelerated by a solution of $\text{K}_3\text{Fe}(\text{CN})_6$ which has been previously exposed to light. The phenomenon appears to be due to the formation of a heterogenous catalyst, which reacts with H_2O_2 . Possibly colloidal ferric hydroxide is formed, which accelerates the thermal decomposition of H_2O_2 , and the formation of a colloid is confirmed by ultramicroscopic observations.

A photochemical after-effect was also observed in the polymerization of styrol (Stobbe), and in the oxidation of several organic substances by free oxygen. Thus, Trautz and Thomas (*Physikal. Z.* **7**, 899 (1906); *Z. wiss. Phot.* **4**, 352 (1906); *Z. Elektrochem.* **13**, 550 (1907)) have noted an after-effect of illumination in the photo-oxidation of sodium sulphide, cuprous chloride in hydrochloric acid solution, and benzaldehyde.

Ghosh and Purkayastha (*J. Indian Chem. Soc.* **2**, 261 (1925); **4**, 409, 553 (1927)) have observed the phenomenon of after-effect in the bromination of cinnamic acid and stilbene. Purkayastha (*ibid.* **5**, 721 (1928)) has suggested that the after-effect is due to the existence of chain reactions, and Weigert's suggestion (*Ann. Physik.* **24**, 243 (1907)) that intermediate complexes or intra-molecular transformation of the light absorbing substances may serve as reaction nuclei in photochemical reactions is in line with this view. Unfortunately there is hardly any experimental fact in favour of the view of intermediate complex formation. Genthe has stated that a strong previous illumination notably accelerates the velocity with which linseed oil takes up oxygen and hardens in the dark. This phenomenon is utilized in industry.

When a mixture of chlorine and hydrogen is illuminated for a short time by an electric spark, a brisk expansion, followed by an immediate contraction, is produced. This phenomenon, known as Draper effect, has been investigated by several workers. Mellor and Anderson (*J. Chem. Soc.* **81**, 44 (1902)), and Burgess and Chapman (*ibid.* **89**, 1402 (1906)), came to the conclusion that the dilation is due to the heating produced by the heat given out in the reaction. This phenomenon has been utilized by Weigert and Kellermann (*Z. physik. Chem.* **107**, 1 (1923)) for showing the preliminary stage in the photochemical combination of hydrogen and chlorine. A glass tube containing a gaseous mixture was traversed by a narrow beam of light given out by an electric spark. On the passage of the ray,

the gas was subjected to dilatation, and this gave rise to a wave visible in a Töpler apparatus. This wave appeared after only $1/100$ of a second after illumination, after $1/40$ of a second was at its best, and it disappeared after $1/10$ second. This wave is not visible in pure chlorine. The dilatation, which constitutes the Draper effect, is then due to the heat given out in the post-photochemical phenomenon, which is only observed after a short time of the illumination and when practically the total amount of HCl has been formed. If the quantum yield, which is ordinarily 20,000 molecules of HCl per quantum, is taken into account, the interval between two successive reactions proves to be of the order 10^{-6} sec. The chlorine which has been illuminated soon loses its activity. Draper thought that HCl was formed when illuminated chlorine was mixed with hydrogen in the dark, but subsequent workers could not verify this statement of Draper. According to the measurements of Le Blanc and Volmer (*Z. Elektrochem.* **20**, 494 (1914)), the duration of the active chlorine is of the order of $1/1000$ sec., whilst Bodenstein and Taylor (*Z. Elektrochem.* **22**, 54 (1916)) found it to be less than $1/1600$ second, and Marshall (*J. Phys. Chem.* **30**, 757 (1926)) gave the limit $1/3000$ second. In view of these observations, the results of Weigert and Kellermann are rather surprising. The presence of hydrogen stabilizes active chlorine. It should be remarked that the chain of reactions as suggested by Nernst does not contemplate the increase of the concentration of atomic chlorine in the stationary state.

In recent communications, Mukerji and Dhar (*J. Indian Chem. Soc.* **3**, 227 (1926); **5**, 203 (1928)) have shown that the phenomenon of "after-effect" is of common occurrence in photochemical reactions. They have observed this phenomenon in the following photochemical reactions: (1) potassium oxalate and iodine, (2) tartaric acid and bromine, (3) lactic acid and bromine, (4) malic acid and bromine, (5) oxalic acid and bromine, (6) citric acid and bromine, (7) potassium formate and iodine, (8) sodium citrate and iodine, (9) oxalic acid, chromic acid, and manganous sulphate, (10) oxalic acid, potassium permanganate, and manganous sulphate, (11) potassium persulphate and potassium iodide, (12) ferrous sulphate and iodine, (13) oxalic acid and iodine, (14) sodium nitrite and iodine, (15) the bleaching of dicyanin, (16) sodium malate and iodine, (17) sodium formate and mercuric chloride, (18) sodium lactate and iodine, (19) decomposition of Fehling's solution in presence of ferric chloride, (20) decomposition of cupri-ammonium oxalate in presence of ferric chloride, and (21) decomposition of potassium manganioxalate.

It was observed by Stark (*Ann. Phys.* **14**, 520 (1904)), Lord Rayleigh (*Proc. Roy. Soc. A* **90**, 364 (1914); **91**, 92 (1914); **108**, 262 (1925)), and others, that a stream of mercury vapour allowed to distil away from the arc or glow discharge in a vacuum remains luminous. Phillips (*Proc. Roy. Soc. A* **89**, 42 (1913)) exposed mercury vapour in a quartz tube to radiations, containing 2537 \AA , from a mercury lamp. He observed that the vapour of mercury began to fluoresce, and he noted that the glow passed up the tube and spread out to a distance of 18 inches from the place of illumination. Franck and Grotian (*Z. Physik.* **4**, 89 (1921)) have repeated the experiment of Phillips, and have accounted for the persistence of the luminosity by supposing that the excited atoms, which have absorbed $\lambda = 2537 \text{ \AA}$, and are prepared to re-emit this line, unite with other mercury atoms to form molecules. When these molecules are again dissociated the stored energy can be liberated and $\lambda = 2537 \text{ \AA}$ is emitted. Recently Asterblum (*Z. Physik.* **43**, 427 (1927)) has shown that the duration of the afterglow of mercury decreases in intensity logarithmically with time. This persistence of the glow in mercury, and the phenomenon of aftereffect as observed in photochemical reactions, appear to be identical.

By applying Turner's expression (*Phys. Rev.* **23**, 464 (1924)) to the photochemical and thermal reactions, the life periods of activated molecules have been calculated by Dhar and Mukerji (*Z. Elektrochem.* **31**, 283 (1925)). The average life of the excited molecules is of the order of 10^{-8} or 10^{-9} second. This order of life period is the same as those experimentally determined by Wien (*Ann. Physik.* **60** (4), 597 (1919)) and theoretically obtained by Milne (*Monthly Notices, Roy. Astronom. Soc.* **84**, No. 5, 354 (1924)) and others, in various cases of activated atoms and molecules.

Wood (*Proc. Roy. Soc. A* **99**, 362 (1921)) has come to the conclusion that though the normal life period of activated atoms and molecules is of the order 10^{-8} second, in some cases the life period can be considerably prolonged, and in several cases it comes out to be of the order 10^{-4} second. We are also of the opinion that the life period of the activated molecules in photochemical reactions taking place in solution is considerably prolonged. The gradual vanishing of the influence of the activated molecules, just after the removal of the reacting system from light to darkness, is evident by a concomitant decrease in the velocity of the reaction, till it has the same value as that obtained in the reaction taking place all along in the dark. Recently, Eggert and his co-workers (*Z. Physik.* **26**, 865 (1925)) have

stated that excited bromine molecules have a relatively long life period, which is possibly of the order of 10^{-5} second. We are of the opinion that the life period of the activated molecules in photochemical reactions taking place in solution is considerably prolonged, and that the slow reversion of the activated molecules into the inactive state is the main cause of the phenomenon of after-effect in photochemical reactions. Hence, because of the prolongation of the life periods of the active molecules, the reactions in question will appear to have a chain mechanism and intermediate stages.

RETARDING ACTION OF LIGHT.

Light in certain cases appears to have a retarding influence. This phenomenon has been observed by Chastaing (1877) in different oxidations in ultra-violet light. Trautz and Thomas (*Physik. Z.* **7**, 899 (1906)) have made a detailed investigation of some of these oxidation reactions in red and violet radiations. Their results were noted by the diminution of the volume of oxygen, and were as follows:

Reactions	Velocity in Dark	Velocity in Red light	Velocity in Violet light
1. $\text{Na}_2\text{S} + \text{O}_2$	239	302	160
2. Ammoniacal solution of $\text{Cu}_2\text{Cl}_2 + \text{O}_2$	254	270	190
3. HCl solution of $\text{Cu}_2\text{Cl}_2 + \text{O}_2$	211	164	59
4. Alkaline solution of pyrogallol + O_2	23	194	27
5. Pyrogallol + O_2	70	77.5	55
6. Benzaldehyde + O_2	20	15	350

Trautz and Thomas observed that for reactions 1, 3, and 6 there is photochemical after-effect, that is, the inhibiting action of light persists partially in the dark. It appears probable from the above results that light decreases the reactional aptitude of the molecules; its retarding influence on a chemical transformation is probably indirect. It can be conceived in particular that light paralyzes a reaction by destroying a positive catalyst, or giving rise to a negative catalyst. The reactions studied by Trautz are exclusively oxidation processes, with the help of free oxygen. It is possible that light can in certain cases decompose the intermediate peroxides formed in these oxidations, with the formation of the original substance, and hence appears to retard the reaction.

Allmand and Maddison (*J. Chem. Soc.* 650 (1927)) have carried out experiments on the oxidation of solutions of sodium sulphite when exposed to light of various wavelengths and in the dark, and have concluded that light of ordinary wavelength has no effect on the velocity of oxidation of an aqueous solution of sodium sulphite.

It appears that light does not retard any chemical reaction (compare Mukerji and Dhar, *Z. Elektrochem.* **32**, 501 (1926)), and the results of Trautz and Thomas need confirmation.

CHAPTER XXV.

Action of Light on Colloids and Periodic Precipitation.

A great deal of experimental work has been recorded on the action of ultra-violet light, β - and X-rays on substances of a colloidal nature (compare Carey-Lea, "Kolloidales Silber und die Photohaloide"; Doelter, "Das Radium und die Farben"; Henri and Mayer (*Compt. rend.* **138**, 521 (1903)); Jorissen and Woudstra (*Koll. Z.* **8**, 8 (1911)); Farmer and Parker (*J. Amer. Chem. Soc.* **35**, 1524 (1913)); Long (*Koll. Z.* **14**, 136 (1914)); Stintzing (*Kolloidchem. Beihefte* **6**, 231 (1914)); Schaum (*Koll. Z.* **15**, 103 (1914)); Nordenson (*Z. physik. Chem.* **90**, 603 (1915)); Pihlbald (*ibid.* **92**, 471 (1917)). Systematic work on the photochemistry of colloids is, however, lacking. The majority of workers have observed a coagulating influence of the radiations on colloids. Thus Galecki (*Koll. Z.* **10**, 149 (1912)) has reported that a gold sol prepared by Zsigmondy's formaldehyde method was coagulated by X-rays. Henri and Mayer (*loc. cit.*), and Jorissen and Woudstra, observed that β -rays from radium can coagulate positive sols like ferric hydroxide, but not negative sols. Fernau and Pauli (*Biochem. Z.* **70**, 426 (1915); *Koll. Z.* **20**, 20 (1917)) studied the coagulation of positive ceric hydroxide sol under the action of radium rays. Schwarz and Friedrich (*Ber.* **55** (B), 1040 (1922)) have observed that the catalytic decomposition of hydrogen peroxide in the presence of colloidal platinum is retarded by X-rays. Catalase is also altered in such a manner by X-rays that its power to catalyse the decomposition of hydrogen peroxide is lessened, though as with the platinum sol, the enzyme recovers its action completely after several hours.

According to Schwarz and Friedrich, the cause of the phenomenon does not appear to lie in the coagulation, diminution in the degree of dispersity, or alteration in the charge of the particles, because the irradiated sol recovers its activity completely within 16 hours. They advance the view that the platinum sol on exposure to X-rays suffers a reversible change at its surface, which must be attributed to the presence of water.

We shall now confine our attention mainly to the action of visible and ultra-violet light on colloids prepared in the laboratory, and those

occurring in nature. Farmer and Parker (*loc. cit.*) and Spear, Jones, Neave, and Shagler (*J. Amer. Chem. Soc.* **43**, 1385 (1921)) have observed that ultra-violet light from a quartz mercury vapour lamp will precipitate colloidal platinum from solutions that are free from electrolyte except the carbonic acid of the air. When electrolytes are present, their precipitating effect on colloidal platinum is greatly accelerated by the action of ultra-violet rays. Moreover Spear, Jones, Neave, and Shagler have shown that the influence of ultra-violet light is greater in dilute solutions of colloids than in those more concentrated.

Some interesting results were obtained by Young and Pingree (*J. Phys. Chem.* **17**, 657 (1913)) on the influence of light from a carbon arc on different positively and negatively charged colloids. They observed that the cataphoretic movement of sols like ferric hydroxide, arsenious sulphide, etc. decreases on illumination, whilst sols of mastic, common rosin, and chlorophyll, show increased cataphoretic movement when exposed to light.

Long (*Koll. Z.* **14**, 136 (1914)) has shown that highly disperse colloidal silver, adsorbed by filter paper and exposed to ultra-violet light, coagulates readily. Siedentopf (*Koll. Z.* **6**, 3 (1910)) has noted the decolorization of the micellae of gold and platinum sols under strong illumination in the cardioid ultramicroscope.

René Audubert (*J. Alexander's Colloid-Chemistry*, Vol. I, p. 353 (1926)) has studied the action of light on suspensions, but his conclusions are not very definite.

Freundlich and Nathansohn (*Koll. Z.* **28**, 258 (1921)) have observed that a diluted sol of arsenious sulphide becomes turbid and unstable towards electrolytes on illumination with a nitra lamp. According to Freundlich and Nathansohn, on illumination, a very highly disperse sulphur sol is formed, probably by oxidation of the sulphide. Moreover, Murphy and Mathews (*J. Amer. Chem. Soc.* **45**, 16 (1923)) have noticed that, on ageing in the dark or on exposure to light, the amount of free sulphur in arsenious sulphide sol increases, and that the electric conductivity markedly increases on exposure to light. Boutaric and Manière (*Bull. Acad. Roy. Belg.* (5) **10**, 571 (1928)) have reported that blue and not red light helps the coagulation of arsenious sulphide sol.

Ganguly and Dhar (*Koll. Z.* **31**, 16 (1922)) have investigated the influence of sunlight on colloidal gold, silver, platinum, copper, sulphur, selenium, a number of colloidal sulphides, hydroxides, and complex colloidal solutions, both in the presence and absence of protecting colloids. In most cases, light has been found to exert a coagulating influence. It has been observed that several sulphide sols, when acted upon by sun-

light in presence of air, are oxidized with the formation of colloidal sulphur, which on further action of light is coagulated.

Recently, systematic work on the influence of radiations of different wavelengths on the properties of several colloids has been undertaken by us. The coagulation, electric conductivity, absorption spectrum, and extinction coefficient have been determined with several positively and negatively charged sols before and after exposure to light. The absorption spectra were measured by a large Hilger quartz spectrograph, and the extinction coefficients were determined by a Hilger Nutting spectrophotometer (compare Miss S. Roy and N. R. Dhar, *J. Phys. Chem.* **34**, 122 (1930) and Miss S. Roy (*J. Indian Chem. Soc.* **6**, 431 (1929)). Our conclusions are recorded below: Coagulation experiments show that sols of ferric hydroxide, chromium hydroxide, zirconium hydroxide, ceric hydroxide (prepared in the hot condition), vanadium pentoxide, manganese dioxide, stannic hydroxide, aluminium hydroxide, thorium hydroxide, and mercuric sulphide become less stable towards electrolytes on exposure to light.

On the other hand, mastic and gum dammar are stabilized on exposure to light. Arsenious sulphide, antimony sulphide, uranium ferrocyanide, cupric ferrocyanide, and prussian blue, when exposed to light for a short time, become stable as regards their coagulation by electrolytes, but on longer exposure they become unstable.

Ceric hydroxide sols prepared in the hot and cold conditions, Odën sulphur sols prepared in excess of acid or thiosulphate, manganese dioxide sol, dilute cupric ferrocyanide sol, uranium ferrocyanide sol, antimony sulphide and mercuric sulphide sols coagulate completely on prolonged exposure to light.

Exposed sols of ferric hydroxide, chromic hydroxide, zirconium hydroxide, ceric hydroxide, stannic hydroxide, aluminium hydroxide, thorium hydroxide, manganese dioxide, arsenious sulphide, antimony sulphide, mercury sulphide, prussian blue, and cupric ferrocyanide are more electrically conducting than the respective unexposed sols. The specific conductivity of vanadium pentoxide, gum dammar, and mastic decreases on exposure.

The absorption spectra show more marked absorption of light in the cases of exposed sols of ferric hydroxide, arsenious sulphide, and prussian blue, and less absorption in the cases of gum dammar and mastic. Measurements of extinction coefficients of sols, however, show that in some cases the exposed sols show more absorption of light than the unexposed ones. No general conclusion has been drawn regarding light absorption of sols on exposure to light.

In most cases the effect of light on sols is in the same direction as that of ageing. The light effect is much more pronounced than the time effect.

The coagulation of a sol by light is due to two causes: (1) decomposition of the stabilizing ion and (2) loss of reactivity of the particles. The former is possibly the more important reason. Recently Panna Lal and Ganguly (*J. Indian Chem. Soc.* **6**, 547 (1929)) have come to the same conclusions working with different sols in ultra-violet light.

In recent years, considerable interest has been shown regarding influence of light on Liesegang ring formation. Küster (*Kolloid. Z.* **13**, 192 (1913)) was the first to observe the influence of light on bands of silver dichromate and silver chloride. Hatschek (*Proc. Roy. Soc. A* **99**, 496 (1921)) has observed that in daylight in many cases there are wide spaces between sets of bands of lead chromate and dichromate in agar, but that in the dark normal bands developed. The ordinary and anomalous bands could be made side by side in the same gel by screening one side and illuminating the other. Such secondary bands have been obtained by Tryhorn and Blacktin (*Trans. Faraday Soc.* **19**, 433 (1923)) with silver dichromate and mercuric iodide. Liesegang (*Kolloid. Z.* **32**, 263 (1923)) has suggested that the effects ascribed to light by Hatschek may be due to difference in temperature.

Davies (*J. Amer. Chem. Soc.* **45**, 2261 (1923)) has reported that light accelerates the production of coloured bands of colloidal gold in silicic acid gels containing gold chloride and various reducing agents.

Dhar and Chatterji (*Koll. Z.* **37**, 3, 89 (1925); **40**, 97 (1926)) have shown that in the formation of periodic precipitates (Liesegang rings) of mercuric iodide, lead iodide, lead chromate, and other substances in gelatine, agar, starch, silicic acid, etc. as media, the number of rings produced in light is much greater than in the dark. Dhar and Chatterji have suggested that in presence of light the coagulation of the sparingly soluble substances, e.g. lead iodide, mercuric iodide, etc. which exist in the colloidal condition in agar, starch, and gelatine, is facilitated, and hence in light there are more rings, which are caused by the coagulation of the sparingly soluble substances, than in the dark.

Blair (*Phil. Mag.* **49**, 90 (1925)) has observed that in the formation of Liesegang rings, intense white light causes irregular rings, and the distance from the top or the source to the last ring decreases. Diminution of this distance is greater in blue than in red light of the same intensity. Ultra-violet light from a quartz mercury lamp renders a gel incapable of Liesegang ring formation. The action of visible light appears to be irreversible, and re-liquefaction and re-setting of the gel

do not relieve the anomalous ring formation. The effect of ultra-violet light, however, does not persist.

Since it is now known that light exerts a modifying influence on periodic precipitation, Hatschek (*Proc. Roy. Soc. A* **99**, 496 (1921)) and Davies (*J. Amer. Chem. Soc.* **44**, 2698 (1922)) have suggested that many naturally occurring rhythmic structures may be the result of alternating day and night rather than due to any inherent periodicity.

PHOTOPHORESIS.

Under the influence of light certain sols show the phenomenon of photophoresis, in which they move in a definite direction. When the colloid particles move towards the light, the phenomenon is positive photophoresis, and when the particles move away from light, it is negative photophoresis. Stintzing (*Kolloid. Chem. Beiheft.* **6**, 231 (1914)) investigated a case in which under the influence of light coagulation and photophoresis of a sol were combined. Silver resinate, dissolved in oil of lavender or benzene, is colloidal, and when illuminated, preferably by ultra-violet light, it coagulates and is deposited preferentially at the illuminated points. S. Roy (*Koll. Z.* **45**, 7 (1929)) has observed streaming of the particles from one side when oil emulsion in water and suspensions of sulphur are illuminated.

Light influences the stability of mist or smoke. The pressure of radiation drives the particles in the direction of radiation. Arrhenius (*Physik. Z.* **2**, 81, 97 (1900)) explains the deflection of the tails of comets by the radiation of the sun, and Nichols and Hull (*Astrophys. J.* **17**, 352 (1903)) have shown that fine soot falling in a vacuum may be deflected from a vertical path by the action of powerful light. Ehrenhaft (*Physik. Z.* **18**, 359 (1917)) has observed a negative photophoresis with finely divided particles of sulphur, selenium and other substances in pure argon, i.e. they moved against the light on illumination (compare, however, Rubinowicks (*Ann. d. Physik.* (4) **62**, 691, 716 (1920); Miss Laski and Zerner (*Z. Physik.* **3**, 224 (1920); Ray (*Ann. d. Physik* (4) **66**, 71 (1921); Gerlach and Westphal (*Verh. d. Deutsch. Phys. Ges.* **21**, 218 (1919); Golsen (*Ann. d. Physik* (4) **73**, 624 (1924)). Schaum and Friederich (*Z. wiss. Phot.* **23**, 98 (1924)) failed to detect any systematic change in the electrophoretic velocities of several metallic colloids suspended in water and organic solvents, under the action of visible and ultra-violet rays. On the other hand, cataphoresis of sols of silver halides is appreciably affected by light, which can bring about reversal of the direction of migration.

PREPARATION OF COLLOIDS BY LIGHT.

Light has been utilized in the preparation of colloids of various substances. Svedberg (*Ber.* **42**, 4375 (1909); *Koll. Z.* **6**, 129, 238 (1910)) has reported that when a metal from which the colloidal solution is to be prepared, and the surface of which has been freed from oxide, is placed in a flat dish, covered with the dispersion medium, and submitted to the action of ultra-violet radiation from a Heraeus quartz mercury vapour lamp, a colloid is obtained. Silver, copper, tin, and lead readily yield colloidal solutions in this way, whereas platinum, aluminium, and cadmium do not. The quantity of the colloidal metal formed is proportional to the amount of radiation which falls on the surface of the metal. The mean size of the colloidal particles increases with increase in the time of exposure to the active rays. This is very likely due to the aggregation of the small particles, which are first formed under the influence of light. It appears from the results of Svedberg, that radiations of wavelengths greater than 4100 Å are incapable of forming colloids according to the above method (Compare Kimura, *Kyoto Mem.* **5**, 257 (1914)). Moreover Svedberg showed that if a solution of chloroauric acid is made alkaline, and reduced by hydrazine hydrochloride in the presence and absence of ultra-violet rays, the colloidal gold which is obtained consists of very much smaller particles in the former case. F. Hartwagner (*Kolloid. Z.* **16**, 79 (1915)) has reported that the formation of gold sol from an alcoholic solution of gold chloride, or from a mixture of gold chloride and hexamethylene tetramine, is accelerated by sunlight.

H. Nordensen (*Koll. Chem. Beihefte.* **7**, 110 (1915)) however, has shown that light, X-rays, and radium rays have no effect beyond that of accelerating the changes which take place in the absence of these rays. Gold and platinum are entirely unacted upon. The colloid formation is ascribed to the photochemical formation of hydrogen peroxide, which attacks the metal, yielding an oxide or hydroxide, which is assumed to dissolve and then be converted to a metallic colloid by the reducing action of the ultra-violet rays. Consequently, there appears to be considerable difference of opinion regarding the mechanism of the formation of colloids by light.

Zwaardemaker and Hogewind (*Proc. K. Akad. Wetensch. Amsterdam* **21**, 131 (1918)) have observed that solutions of several odorous substances like eugenol, cresol, safrole etc., on keeping for several weeks, passed into the colloidal condition, and that this action is accelerated by sunlight and ultra-violet rays. Moreover, we have shown that the for-

mation of colloidal ferric hydroxide from ferric chloride, and ceric hydroxide from ceric ammonium nitrate, by hydrolysis is also accelerated by light.

Dede and Walther (*Ber.* **58**, B, 99 (1925)) obtained colloidal arsenic by passing purified arsine through water exposed to ultra-violet rays. According to the dilution, these sols are yellow to bluish violet in colour. The particles are negatively charged, and are not sensitive towards electrolytes.

INFLUENCE OF LIGHT ON BIO-COLLOIDS.

We shall now consider the influence of light on some bio-colloids. The action of ultra-violet rays on living cells has been investigated by Bovie (*Science* **24**, 374 (1913)). He has reported that fresh egg albumin, when exposed in a quartz vessel at a distance of 10 centimeters from a quartz mercury vapour lamp at the room temperature, begins to coagulate in about $1\frac{1}{2}$ hours on the wall nearest the lamp, and that after 35 hours the coagulation is complete. Dilution with water or addition of ammonium sulphate helps the photo-coagulation of albumin. Ox serum is coagulated when exposed to ultra-violet radiation in quartz vessels, but not in glass vessels. The coagulated material obtained in light resembles the product obtained by heat coagulation, and it is insoluble in alcohol, water, and dilute acids, but is soluble in dilute alkalis. Moreover, Bovie and collaborators (*J. General Physiology* **1**, 323, 331 (1919); *Amer. J. Physiol.* **66**, 55 (1923)) have studied the influence of ultra-violet radiation on *paramecium candatum*, and have observed marked cytolysis even after a short exposure.

Koertz (*Biochem. Z.* **137**, 372 (1923)) has attempted to find out a relation between the physico-chemical condition of the cell colloids and their light sensitiveness, and has come to the conclusion that irradiation affects the cell protein rather than surface colloids. Clark (*Amer. J. Physiol.* **61**, 72 (1922); *Amer. J. Hyg.* **2**, 322 (1922)) has observed that ultra-violet light causes aggregation and flocculation of egg albumin of p_H 4.8 (negatively charged). When the albumin is uncharged or positively charged, a greater state of dispersion seems to arise. Howell (*Arch. intern.* **18**, 269 (1921)) has reported that the precipitation of fibrinogen by ultra-violet light is inhibited by the presence of hemato-porphyrin, which acts as a sensitizer and converts fibrinogen into a more soluble protein.

Burge (*Amer. J. Physiol.* **39**, 335 (1916)) has concluded that radiation changes cell protoplasm in such a manner that certain salts can

combine with it and form a precipitate. Burge observed that large quantities of calcium salts or sodium silicate in the cells of the eyelids or cornea increased the inflammatory action of the radiation. By exposing fish living in dilute solutions of calcium salts or sodium silicate to ultra-violet rays, Burge was able to produce cataract.

Mond (*Pflüger's Archiv* **196**, 540 (1922)) has shown that ultra-violet radiation increases the stability of globulin and fibrinogen colloids, whilst the stability of globulin is diminished. Exposure of crystallized serum and egg albumins at various hydrogen ion concentrations to ultraviolet radiations causes a shifting of the p_H towards the acid side in solution with a $p_H < 4.6$, and towards the alkaline side in solutions of $p_H < 4.3$. With lecithin suspensions, exposure increases the acidity.

According to Noak (*Z. Botan.* **12**, 273 (1920)) the influence of light on cells is exerted through the agency of substances which convert the light energy into chemical energy. Fluorescent organic compounds and salts of heavy metals act as catalysts in this transformation of light into chemical energy, by acting as carriers of oxygen.

Schanz (*Arch. ges. Physiol.* **164**, 445 (1916)) has found that by the action of ultraviolet rays on egg and serum proteins, in alkaline solution, the amount of substances precipitated by ammonium sulphate and sodium chloride was decreased; while in acid solution, the amount precipitated was increased. The change produced by light is regarded as gelatinization of the proteins, and it is accelerated by oxygen. Kreibich (*Arch. Path. Anat. (Virchow)* **222**, 28 (1916)) has reported that ultra-violet rays render proteins insoluble. This, in the case of cells, causes catalase to become more firmly bound, and this leads to the retardation of catalase action and results in pyknosis and hyaline degeneration.

Moreover, Schanz (*Pflüger's Archiv* **170**, 646 (1918)) came to the conclusion, from observations on the lens of the eye, that the effect of light is to render protein less soluble. Schanz has observed that in diabetes there is frequent occurrence of the opacity of the eye lenses, and acetone is formed. His experiments on the action of sunlight on proteins in presence of acetone showed that the precipitation of proteins by light is increased by acetone.

Recently, Spiegel-Adolf (*Klin. Woch.* **7**, 1592 (1928)) has reported that when serum albumin, serum, other blood proteins, and egg albumin are exposed to ultra-violet light, they show an increased absorption of ultra-violet radiations. Moreover, Fernau and Spiegel-Adolf (*Biochem. Z.* **204**, 14 (1929)) have shown that freshly electro-dialyzed serum albumin, kept under toluene, loses its power of coagulation by exposure to

light and radium emanations, probably owing to the formation of ammonia.

Spiegel-Adolf (*Strahlenther.* **29**, 367 (1928)) has stated that the velocity of coagulation of proteins in radiations from a mercury vapour lamp is markedly affected by the presence of traces of electrolytes, and by the age of the solution after electro-dialysis. It has been observed that below a certain concentration, the exposure necessary for a visible change increases with the dilution; in more concentrated solutions the outer layers protect the inner.

CHAPTER XXVI.

Action of Linearly Polarized Light.

The results obtained with the action of polarized light in photochemical phenomena are very few. According to Weigert (*Z. Elektrochem.* **24**, 222 (1918)) the phototropic sensitiveness of tetrachloro- α -cetonaphthalene varies with the orientation of the plane of polarization of the light relative to the axes of crystals. Similar observations have been made by Padoa, who has reported that the direction of the plane of polarization has no influence on the velocity with which crystalline cinnamic acid is transformed into its dipolymer α -truxillic acid. The transformation of ortho-nitrobenzaldehyde to o-nitrosobenzoic acid, and that of cinnamylidene malonic acid (dipolymerization) are on the contrary inequally sensitive to polarized rays which are either parallel or perpendicular to the axes of the crystal. If these two substances are powdered, their photochemical sensitivity, as has been stated by Bowen, is the same for the polarized as for unpolarized light.

It can be concluded from the few experimental facts, that the direction of the plane of polarization has only a quantitative influence in the photochemical transformation of a crystal. If, for example, polarized light acts in different directions on a crystal of β -tetrachloro- α -cetonaphthalene, the transformation is more or less rapid, but does not vary qualitatively, and from an examination of the changes undergone it cannot be recognised whether the light is polarized or not. When the photosensitive substance is not crystalline, the case becomes different. According to the experiments of Weigert (*Z. Physik.* **5**, 410 (1921)); *Z. physik. Chem.* **100**, 537, **101**, 415 (1922); **102**, 416 (1922)) polarized light can produce special effects. Thus, if silver chloride is submitted to the action of coloured rays, after being exposed for a short time to white light, it becomes green in green light, yellow in yellow light etc. It has now been established that these differently coloured silver halides are not different chemical substances, but that the different colours are due to difference in the sizes and numbers of the particles of colloidal silver disseminated in the silver chloride. These differently coloured silver chlorides have been obtained without the intervention

of light, by the action of chlorine on a thin layer of metallic silver placed on a glass or mica plate. Weigert has stated that polarized rays of different colours act on a layer of photochloride not only by modifying the colour but also by producing anisotropy, which is manifested by a durable dichroism.

The phenomenon is complicated, and the dichroism changes with the duration of the illumination, and can have a maximum and a minimum. The variations are not the same for red, yellow and green rays.

Zocher and Coper (*Z. physik. Chem.* **132**, 303 (1928)) have shown that under the influence of linearly polarized light, sensitive silver chloride similar to that studied by Weigert, but without any binding material such as gelatin, becomes dichroic and doubly refracting. Many of the other photosensitive systems do not undergo this change, but sensitive films of cuprous bromide have also been prepared. In the case of silver, it seems probable that anisotropy arises from the elongated form of the colloidal particles of metal.

Recently, Zocher and Coper (*Z. physik. Chem.* **141**, 217 (1929)) have claimed that the Weigert effect already discussed, which has been so far observed with red light, can also be obtained with white light. When layers of light-sensitive material are illuminated with linearly polarized light, they become anisotropic and exhibit the phenomenon of dichroism. Recently, Weigert (*Z. physik. Chem. B.* **3**, 377, 389 (1929); **B 4**, 83 (1929)) has classified the experimental data of this phenomenon, which appears to be very complex, as cases of "photodichroism" and "photoanisotropy". Three different effects appear to be present: primary, secondary, and induced photodichroism or photoanisotropy. Induced photodichroism appears to be a new phenomenon, which consists of the presence in a primary photoanisotropic system of new coloured particles which show photodichroism. It is stated by Weigert that the phenomenon of photodichroism can be obtained pure and without distortion, in a photographic layer exposed to polarized light, with the simultaneous occurrence of primary and secondary photodichroism, if, after exposure, the layer is fixed, and the coloured silver particles are produced by physical development. It has been asserted by Weigert that the phenomenon of induced photodichroism is of the same general nature as primary photodichroism, and can be produced in almost all light-sensitive colouring matters in layers.

Weigert and Elvegard (*Z. physik. Chem. B.* **4**, 239 (1929)) have investigated the primary photodichroism when caused by monochromatic light, using more accurate apparatus. The existence of a selective effect of the dichroism in the excited layer, varying with the wavelength

of the light used, was shown with certainty. The curves obtained for radiations of long wavelengths are different from those with short wavelengths.

Weigert and Nakashima (*ibid.* B. 4, 258 (1929)) have concluded from the form of the dichroism curve that polarized light has two different actions. For weak excitation there is a very sharp colour selectivity. The special form of the extinction curve for any particular colouring matter does not influence the dichroism. For strong excitation, the extinction curve of the colouring matter is important. It is concluded that in light-sensitive colouring matters, two different phenomena occur by the action of light, and they can be separated from each other by the method of dichroism.

Polarized light also produces an anisotropy in layers of collodion containing cyanin. The phenomenon is less clear and more complicated than that obtained with the photochloride of silver, because in the case of cyanin the bleaching effect on the colouring matter by light is superposed upon the dichroic effect of light.

In the photochlorides not containing soluble salts, according to Weigert, light produces no chemical change. The quantity of free silver remains constant and its partition in silver chloride is only modified. A quantum of light will simply shift an electron from an atom to an ion of silver. On the other hand, under the action of polarized light, the electron is only displaced in a definite direction, and thus that a polarized quantum can react, it is necessary, not only that the silver atom and the silver ion Ag^+ , should be at a suitable distance, but that the line connecting these two should be in a desired direction. In the beginning there is complete disorder in the re-partition of the silver atom and the silver ion, and the system is consequently sensitive to a large spectral region, and its sensitiveness is independent of the direction of the plane of polarization. But when the monochromatic and polarized light has acted for a certain time, the particles which are favourably situated have taken part in the absorption and are modified, and cannot take part in the absorption as before. The transparency of the layer to the exciting radiations is increased, and thus Weigert has explained the coloration and dichroism observed with polarized rays.

Recently Cotton (*Compt. rend.* 189, 599, 657 (1929)) has observed the Weigert effect with plates prepared by dipping them after being coated with gelatin containing collargol into a solution of cupric halide. Such a plate exposed to polarized light from an ordinary arc lamp for one hour can be examined in the green light of mercury without fixing, or with

shorter exposure after development. A chloride plate can also be rendered dichroic by exposure for 18 hours to polarized light of wavelength 3660 Å obtained from a mercury lamp with a nickel oxide screen. Cotton prefers to attribute the phenomenon to anisotropy of distribution, rather than to anisotropy of the shape of the ultra-microscopic silver grains, as suggested by Weigert. Cotton has observed no effect of circularly polarized light on the special plates prepared by him or the plates prepared according to the method of Zocher and Coper (*Z. physik. Chem.* **132**, 313 (1928)), when formaldehyde is the reducing agent. The effect described was obtained when lævo- or dextro-tartrate of potassium and sodium was the reducing agent. It is pointed out that there has been no synthesis of active molecules but merely production of an active arrangement of molecules in a medium.

ACTION OF CIRCULARLY POLARIZED LIGHT.

Numerous attempts have been made to synthesize optically active compounds in the laboratory with the help of circularly polarized light. It is well known that, starting with an optically inactive substance, the synthesis of a compound having an asymmetric atom leads to a product which is inactive. This is due to the fact that the molecules of the two optical antipodes have exactly the same stability, and have the same chances of formation from symmetrical molecules.

In plants, however, optically active bodies are formed from simple inactive substances like water, CO₂, nitrates etc. The vegetable cells are only formed from dextro-rotatory-cellulose or d-glucose or d-fructose. Similarly strychnine, brucine, nicotin, quinine, and camphor are generated in only one of the two possible forms. This striking difference between artificial and natural synthesis has to a certain extent been eliminated, and optically active compounds have been obtained in the laboratory starting from inactive substances. In order to realise such an asymmetric synthesis it is necessary to be in possession of an active substance which can intervene in the operations in one of two different ways. It can be utilized for separating the two antipodes which form the racemic mixture. It can also act in the reactions themselves, where a new asymmetric atom is generated, and the formation of one of the two enantiomorphous modifications is favoured. Pasteur was the first to remark that for the realization of a complete synthesis of an active compound, it is necessary to have recourse to the action of physical asymmetry. Curie has stated that these actions should have the enantiomorphous symmetry which characterizes the molecules

of the optically active substances. Now the agents which present this kind of symmetry, and which at the same time have an influence on the chemical reactions are very few. The following may be mentioned:— (1) The combination of an electric and a magnetic field superposed on each other, and having their lines of force parallel, (2) a magnetic field traversed in the direction of the lines of force by a rectilinearly polarized ray of light, (3) circularly polarized light.

Guye and Drouguine (*J. Chim. phys.* **7**, 96 (1909)) have carried out the bromination of fumarate, and cinnamate of methyl in an electric field superimposed upon a magnetic field, but no optically active compounds were obtained. It appears that the action of the circularly polarized light has greater chance of producing optically active substance than the simultaneous action of an electric and magnetic fields. Attempts have been made to utilize the simultaneous action of rectilinearly polarized light and a magnetic field. Cotton (*J. Chim. phys.* **7**, 81 (1909)) has stated that the dextro- and lævo-cupri alkaline tartrates absorb unequally lævo- and dextro-circular rays. A similar behaviour has been observed by Dowell (*Phys. Review* **26**, 162 (1905)) with other optically active substances. We might expect that the two cupri-tartrates are unequally sensitive to the action of polarized light in a definite sense. However, the experiments of Cotton have not confirmed this view. The action of circularly polarized light on a racemic mixture of tartrates did not produce any noticeable optical activity. Byk (*Z. physik. Chem.* **49**, 641 (1904)) was also unsuccessful in similar experiments with Fehling's solution. Similar negative results have been obtained with silver tartrate.

Carboxylic acids decompose in light with the formation of CO_2 in presence of uranyl or ferric salts. Henle and Haakh (*Ber.* **41**, 4261 (1908)) have studied the transformation of methyl-ethyl-cyano-acetic acid to methyl-ethyl-aceto-nitrile, and that of symmetrical dichloro-dimethyl-succinic acid into dichloro-dimethyl-propionic acid, under the action of circularly polarized light, or rectilinearly polarized light under the action of a magnetic field, but only inactive products were obtained. Cherbuliez (*Arch. de Sc. phys. et. nat. Genève* **V**, **17**, 159 (1925)) tried to prepare active dibromophenyl propionic acid by the bromination of cinnamic acid under the action of circularly polarized light, but negative results were obtained. Freundler (*Ber.* **42**, 233 (1909)) studied the decomposition of diamyl acetal racemate of ortho-nitro-benzaldehyde in solution, under the action of circularly polarized light. The experiments of Jaeger on the photolysis of dextro and lævo cobalti-potassium oxalate, and those of Bredig (*Z. angew. Chem.* **36**, 456 (1923)) on

the decomposition of lactic acid, diazo camphor, and complex cobalt compounds containing ethylene diamine, have also yielded negative results. In spite of these failures, it is generally admitted that asymmetric synthesis by the action of circularly polarized light ought to be possible. Recent observations of Zocher and Coper (*Sitzungsb. d. preuss. Akad. d. Wiss.* 426 (1925)), seem to confirm this opinion. These authors have experimented with layers of photochlorides of silver not exactly identical with each other. They have stated that these layers under the action of circularly polarized light undergo an asymmetric change which is manifested by optical activity, as well as by circular dichroism analogous to that observed by Cotton in cupritartrates. It is clear that in these experiments of Zocher and Coper there is no formation of optically active compounds, and the asymmetric elements which are formed are not the molecules. Zocher and Coper have proposed following explanation:— The photochlorides are forms of particles of silver disseminated in the silver chloride. These particles distributed altogether irregularly form very diverse figures; some of them are asymmetric and can be arranged in the left or right directions. If the system is now illuminated by right circularly polarized light, the light is unequally absorbed by the two configurations, right and left, which in the beginning existed in equal numbers. Those which absorb the light most will be altered most. Whatever may be the changes undergone by them, an asymmetry in the structure will be the result, and this will be translated into optical activity and circular dichroism.

Zocher and Coper (*Z. physik. Chem.* 132, 313 (1928)) have reported that by the action of circularly polarized light on a film of sensitive silver chloride, there is formed colloidal silver, which manifests both circular dichroism and circular double refraction.

W. Kuhn and Braun (*Naturwiss.* 17, 227 (1929)) have shown that the rotatory dispersion of ethyl- α -bromo-propionate in the ultra-violet discloses at first an increased rotation (specific rotation in alcohol of about 4000° at 2450 \AA) followed by a reversal. The absorption bands in the near ultra-violet must therefore have influenced powerfully the optical activity, when 4—8% alcoholic solutions of the racemic ester were exposed in quartz flasks to circularly polarized light (monochromatic Mg line 2800 \AA). A solution of the active ester was simultaneously exposed to unpolarized light of corresponding intensity, to provide control for the period of irradiation. The solutions exposed to dextro-circularly polarized light showed dextro-rotation, and *vice versa*. The greatest effect so far observed is 0.05° on either side. The effect observed agrees in sign with theoretical predictions.

CHAPTER XXVII.

Photochemical Decomposition of Halides of Silver and Einstein's Law of Equivalence.

The blackening of silver chloride in light was observed by Fabricius in the 16th century, and possibly by C. Gesner (1565). Boyle (1560) noted that horn silver blackens in air. These observations of Fabricius, Gesner, and Boyle passed unnoticed, and the same phenomenon was rediscovered by the Italian physicist Beccarius in 1756. Scheele, the greatest discoverer of the 18th century, stated that the blackening of silver chloride is accompanied by the liberation of chlorine. A little later, Senebier studied the effect of light of different colours and observed a maximum sensitiveness towards the violet rays, and stated that silver chloride takes up the colour which varies with the exciting light. The same fact was more clearly proved by Seebeck in 1820, who obtained an image of the visible spectrum by its action on silver chloride, which had been made gray by a preliminary exposure to white light. The phenomenon involved in the coloration of silver chloride is reversible. The red coloured products obtained by the action of red light can become blue under the action of blue light. Similar observations have been made with silver bromide. There is considerable difference of opinion regarding the nature of the chemical change involved in the blackening of the silver halides in light. Two main views are favoured by different specialists in this line. Till recently the majority of workers, notably Carey Lea, Luther, Guntz, and Baur have agreed that silver chloride on exposure decomposes into chlorine and a subchloride according to the equation $2 \text{AgCl} \rightarrow \text{Ag}_2\text{Cl} + \text{Cl}$. The differently coloured photochlorides are assumed to be different solid solutions of the subchloride in the normal chloride. On the other hand, Eder (*Photochemie*, page 277 (1904)); Volmer, and specially Trivelli (*Z. wiss. Phot.* **6**, 358 (1908); *Jahrb. d. Radioakt. u. Elek.* **8**, 334 (1911)) have assumed the formation of several distinct subchlorides such as Ag_8Cl_7 , Ag_4Cl_3 , Ag_8Cl_5 , Ag_2Cl etc. in explaining the formation of different coloured products.

The other view, which is supported by Lorenz, Lüppo-Cramer, Sicking, Reinders, Weigert, Noddack, Zsigmondy, Hartung and Svedberg, and others, is that chlorine and silver are liberated in the blackening caused by exposure to light, and that different photochlorides are formed by the dispersion of colloidal silver in the undecomposed silver chloride. Numerous facts observed in the last few years support this view. Lorenz has drawn attention to the analogy between the photohalides and the metallic fog formed in the electrolysis of molten salts. Moreover, Lorenz and Hiege (*Z. anorg. Chem.* **92**, 27 (1915)) have observed the formation of particles visible in the ultramicroscope, and soluble in dilute nitric acid, on exposing pure crystals of the silver halides to light. It seems, therefore, that particles of metallic silver are formed.

Carey-Lea (*Kolloides Silber und die Photohaloide* p. 8 and 29), and several other workers, have been successful in obtaining products resembling the photohalides without the action of light. With this object in view different methods have been adopted, e. g. partial reduction of silver chloride or silver bromide, action of HCl or HBr on a partially reduced silver salt, action of chlorine on colloidal silver or a thin layer of metallic silver. These artificial subhalides are exactly similar to those obtained by the action of light on silver halides; and they are undoubtedly simple mixtures of metallic silver with silver halides. In spite of numerous attempts, it has not been possible to demonstrate the existence of a definite subhalide (Ag_2Cl or Ag_2Br) in these products, and hence Reinders (*Z. physik. Chem.* **77**, 213, 356, and 677 (1911)) came to the conclusion that definite subchlorides are neither formed at the ordinary temperature nor in the molten salt. Reinders obtained the photochloride in the crystalline state by two different methods:

(1) Slow crystallization of silver chloride dissolved in ammonia or concentrated HCl in presence of light, (2) crystallization of an ammoniacal solution of silver chloride containing colloidal silver in the dark. The crystals obtained by these two methods are differently coloured according to the experimental conditions. These photochlorides dissolve in ammonium hydroxide or sodium thiosulphate leaving a residue of metallic silver. Reinders assumes that the diverse colorations of the photohalides are due to differences in the dimensions of the particles of metallic silver. He has observed colour changes on prolonged exposure of silver chlorides similar to those obtained in the formation of colloidal solutions of silver or gold by the action of reducing agents on their salt solutions. Moreover, Wöhler and Krupp (*Ber.* **46**, 2045 (1913)) have studied the coloured products obtained in the photochemical decomposition of silver hydrazoate (AgN_3), and have

shown that these products are simple mixtures of colloidal silver and AgN_3 . It appears, therefore, from the above facts that the photohalides are likely to be simple mixtures of normal halides with small quantities of colloidal silver.

When silver chloride is exposed to light in a sealed tube, its decomposition is stopped when the pressure of the liberated chlorine attains a limiting value. In the dark the liberated chlorine slowly recombines with the metallic silver and disappears. This reaction is also likely to be accelerated by light. The maximum tension of the liberated chlorine depends on the intensity of the light. According to the experiments of Luther (*Z. physik. Chem.* **30**, 628 (1899)), the maximum tension varies from 0.01 to 0.1 atmosphere depending on the intensity of the light. If the liberated chlorine is eliminated, the photochemical decomposition is not stopped by the opposing reaction of chlorine on silver. Hartung (*J. Chem. Soc.* **121**, 682 (1922); **125**, 2198 (1924); **129**, 1349 (1926)), working with a microbalance, showed that *in vacuo* the decomposition of very thin layers of silver halides on illumination for several days in sunlight can be carried out almost quantitatively to completion. The liberated halogen was absorbed either by metallic copper or KOH, in Hartung's experiments. Moreover, he showed that the loss in weight on exposing silver halides to light can be restored by subsequent halogenation. The observations of Hartung have, however, been contradicted by Koch and Schrader (*Z. physik.* **6**, 127 (1921)). The photochemical decomposition of silver bromide is similar to that of silver chloride, and the coloured photobromides have the same constitution as the photochlorides. This decomposition is also reversible, an equilibrium being attained.

The bromide of silver is more photosensitive than the chloride, and its great photosensitivity is utilized in photography. The iodide of silver is less photosensitive than the chloride, and possesses some properties different from those of silver chloride and bromide. Scholl (*Wied. Ann.* **68**, 149 (1899)) observed that if a thin sheet of silvered glass is exposed to iodine vapour, a layer of yellow crystalline and almost transparent silver iodide is formed. In light, this silver iodide remains yellow but becomes turbid and finally opaque. Amorphous silver iodide becomes grayish green on exposure, or even on prolonged illumination, but the amount of iodine liberated is very small. On the other hand, Dhar (*J. Chem. Soc.* **111**, 694 (1917)) showed that large quantities of silver halides, including silver iodide, can be completely decomposed to gray metallic silver when the halides are mixed with ammonium oxalate and exposed to sunlight.

Emulsions used for the preparation of photographic plates and films consist of a colloidal suspension of silver halides, mainly silver bromide with a small amount of silver iodide, in gelatin. The X-ray spectrum of these colloidal particles shows that they have a crystalline structure of a type belonging to the regular system. Recently, accurate information concerning the processes taking place in photographic emulsions on illumination, has been obtained by the microscopic and other investigations carried on notably by Svedberg (*Z. wiss. Phot.* **20**, 38 (1920); *Phot. J.* **61**, 325 (1921); **62**, 180, 310 (1922)); Slade and Higson (*Phot. J.* **59**, 260 (1919); **61**, 35, 144 (1921); *Proc. Roy. Soc.* **98**, A 154 (1920)), the Eastman Kodak Laboratory (Trivelli, Righter and Shepard, *Phot. J.* **62**, 407 (1922); *Scien. Pub. Eastman, Kodak, Res. lab.* **7**, 84 (1924)).

The main results of these researches are as follows:—

(1) The action of light usually makes a grain of the silver halide in an emulsion entirely developable, but the tendency to be developed is limited to the grain itself and is not transmitted to the neighbouring ones. Sometimes, however, a group of grains may act as a unit.

(2) The probability of a grain becoming developable on illumination follows the laws of chance. Larger grains are usually more sensitive than small ones, but if grains from different emulsions are compared, grains of the same size and shape can differ in sensitivity.

(3) The development of the grains starts from certain points — “the centres” — which are visible on the grain as dark spots, if the development is stopped before completion. Each grain which contains at least one centre can be completely developed.

(4) In a group of grains of a given size, the distribution of centres after illumination follows the laws of chance. The number of centres in grains increases with exposure.

(5) The centres are located not only on the surface of the grains but also in their interior. Lüppo-Cramer showed that the ease with which a grain of an illuminated emulsion becomes developed is destroyed by an oxidizing agent, and can be restored by dissolving the surface layer of the halide grains.

(6) Under normal conditions the development starts only from those centres which are on the surface of the grains.

There is difference of opinion regarding the origin of the centres; one view is that the centres are adsorbed silver atoms or groups of atoms, but Toy (*Phil. Mag.* **44**, 352 (1922)) and others advanced the view that the centres exist in the grains before illumination, and that the action of light consists mainly in activating them for developing.

Silberstein (*Phil. Mag.* **44**, 254 (1922)) advanced the view that a centre is formed, and a grain becomes ready to be developed, every time a light quantum ("light dart") hits the surface of the grain. This view becomes untenable in consequence of the experiments of Trivelli and Righter (*Trans. Farad. Soc.* **19**, 296 (1923)), who measured the yield of such collisions in a thin layer of grains, and showed that not more than 0.001 of the exposed area of the grains is sensitive to light. It should be stated that these measurements are not the actual quantum yield, because only the incident light intensity and not the absorbed energy was measured. Also Toy (*Trans. Farad. Soc.* **19**, 1290, (1923)) showed that the sensitivity of an emulsion to decreasing wavelengths does not decrease, as would be expected according to Silberstein's view, but increases towards the ultraviolet, being approximately proportional to the amount of light energy absorbed by the emulsion.

DETERMINATION OF THE QUANTUM YIELD.

In recent years a determination of the quantum yield in the photochemical decomposition of silver halides has been attempted by several workers. Developers for the identification of light action have been avoided, and the silver formed during the photochemical action had to be measured directly. The illuminated emulsion was treated with a fixing solution, thus exposing the silver formed both at the surface and in the interior of the grains. The silver formed was dissolved in nitric acid and was titrated. Unfortunately, different investigators obtained widely varying quantum yields. Weigert and co-workers (*Z. physik. Chem.* **99**, 499 (1922); *Z. Physik* **18**, 232 (1923)) obtained at first a quantum yield very nearly unity under very special conditions, but the photochemical efficiency was much smaller in other conditions. Eggert and Noddack (*Sitzb. Preuss. Akad.* 631 (1921)) stated that the quantum yield decreased below unity only on very intense illumination. The difference between these observations may be due to errors in the measurement of light absorption by the silver halides in a very finely dispersed system, when the scattering of light is greatly increased. Eggert and Noddack observed that only 5—10 % of radiation of wavelength 4080 Å is absorbed by a technical AgBr plate, and they compared the amount of silver formed with this light absorption, and concluded that the quantum yield is approximately unity. On the other hand, Weigert came to the conclusion that about 80% of the light is absorbed under the experimental conditions of Eggert and Noddack, and thus the quantum yield is much lower than unity. Eggert and Noddack

(*Z. physik. Chem.* **20**, 299 (1923); **21**, 264 (1924); **31**, 922 (1925)) confirmed Weigert's value of light absorption, but suggested that absorption was largely due to gelatin, and that only light energy absorbed by silver halides is photochemically active. The measurement of Eggert and Noddack showed that molten silver bromide absorbs light of wavelength shorter than 4660 Å, and molten silver chloride absorbs light shorter than 4050 Å. Moreover, they also measured the absorption of pure silver bromide, and pure silver chloride photographic plates, and of pure gelatin of thickness 1.57 mm. Pure silver bromide photographic plate is sensitive to radiation of wavelength 4660 Å, silver chloride plate to radiation 4050 Å. Pure gelatin of thickness 1.57 mm. shows the following absorption, which varies considerably with the variety of gelatin used:

Wavelength	6150	5460	4900	4360	4050	3650 Å
Absorption	24	32	42	62	88	94 %

Eggert and Noddack also found that ordinary photographic plates show a marked absorption of light from 6150 Å, and that this absorption increases towards the shorter wavelengths. Hence they suggested that the absorption of light by emulsions is mainly due to gelatin, and that the actual path of light in the photographic layer is much longer than the measured thickness because of several reflections of the light by the silver halide particles. Using the above absorption values for gelatin, and assuming the validity of Lambert's law, Eggert and Noddack calculated the following values of light absorption by the gelatin and the silver halide, on the assumption that the absorption of radiation 6150 Å is due entirely to gelatin.

"Agfa reproduction" silver bromide emulsion, and special silver chloride emulsion.

Wavelength Å	% scattered	% transmitted	% absorbed		
			Total	gelatin	halide
6150	60	29	12	12	0
5460	62	24	15	17	—2
4900	61	20	20	23	—3
4360	41	11	48	37	11
4050	23	8	69	53	16
3650	12	4	84	74	10

Weigert criticised these results, and suggested that the absorption coefficients and not the absorption should be used in calculating the partial absorption by gelatin and silver halides, and that the method

adopted by Eggert and Noddack yields values for the absorption of the halides which are too low. The applicability of Lambert's law is also doubtful, because we have to assume an equal scattering power of halide particles for all wavelengths. From the titration of the silver formed photochemically, and a calculation of the number of absorbed quanta, Eggert and Noddack obtained the quantum yield of unity for wavelengths 4360, 4050, and 3660 Å in the case of silver bromide, and for 3660 Å in the case of silver chloride. A slow decomposition of silver chloride in radiations of wavelengths 4360 and 4050 Å was also investigated, and from its velocity it was concluded that if the equivalence law is applicable to this case, about 0.3% of radiation 4360 Å and about 1% of 4050 Å are absorbed by the silver chloride.

The quantum yield in the case of bromide was found to be unchanged within the limits 3.9×10^{15} to 30×10^{15} absorbed quanta per square cm.; with longer exposures the quantum yield decreased to 0.06 for 5×10^{19} quanta absorbed per square cm. After treating the bromide plates with water, alkali, etc. the quantum yield could be maintained equal to unity for larger amounts of absorbed energy. The decrease in the quantum yield for the chloride emulsions was less marked; the same value was obtained between 1.1×10^{15} and 147×10^{15} quanta absorbed per square cm. A slow decomposition of silver iodide emulsions gave a low yield, even for the initial stages of illumination.

Weigert and his co-workers (*Sitzb. Preuss. Akad.* 641 (1921); *Schubert Dissertation*, Leipzig (1923)), working with emulsions containing finely dispersed silver chloride (1 part), and silver nitrate, silver citrate, and silver tartrate distributed in gelatin, obtained an S-shaped curve by plotting the amounts of silver formed against time of illumination. Thus the process is an autocatalytic one. The amount of silver chloride remains unchanged, apparently only the soluble salts being decomposed. From these observations, and the fact that the total absorbed number of quanta was higher than the number of atoms formed, Weigert concluded that silver chloride is not light-sensitive, and that only light absorbed by the metallic silver present acts photochemically. Eggert and Noddack (*Z. Physik* 31, 922, 942 (1925)) could not verify Weigert's observations, and did not get the S-shaped curve. The light absorption of silver chloride was only 5% for the light 3660 Å, and the quantum yield was of the order 1×10^{-2} for 4360 Å, 2×10^{-2} for 4050 Å, and 6×10^{-2} for 3660 Å. Weigert's observation that the amount of silver chloride remained unchanged was explained by Eggert and Noddack on the view that all chlorine atoms formed by the action of light recombined with silver from the soluble silver salts forming silver chloride.

Eggert and Noddack stated that the absorption of one quantum of light energy by a halide particle always results in the decomposition of one silver halide molecule. The halogen atoms are subsequently absorbed by gelatin, or some other acceptor present in the emulsion. Since, with increasing amounts of energy absorption, the acceptors become more and more saturated with halogen atoms, which partly recombine with silver atoms, a decrease in the quantum yield is finally observed. This can be partly avoided by adding water, alkali, etc., which act as acceptors. The influence of acceptors is most energetic when chlorine atoms are formed, less so with bromine, and least with iodine. Hence, in the presence of large amounts of acceptors (as soluble silver salts in daylight photographic papers), visible images can easily be obtained by use of a silver chloride emulsion, but no visible image is obtained with silver bromide or iodide emulsion, as the liberated halogen atoms recombine with silver atoms. There are several difficulties in the views of Eggert and Noddack, who find that the quantum yield is the same for two widely different silver bromide emulsions; but microscopic studies show that the light-sensitiveness of grains in different emulsions varies widely. Moreover, Svedberg, Slade, and Higson obtained S-shaped curves by plotting the number of developed grains against exposure, and these results support the observations of Weigert rather than those of Eggert and Noddack.

According to Helmick (*J. Opt. Soc. Amer.* **9**, 521 (1924)) the quantity of ultra-violet energy required to render a grain of photographic silver bromide developable is as follows: For 2537 Å, the average quanta per grain is 731 ± 14 , for 2653 Å, 514 ± 11 , for 3131 Å, 510 ± 16 , for 3650 Å, 555 ± 13 . It appears that a quantum of smaller energy content is more efficient in the decomposition of silver bromide.

The following observations of Bodenstein (*J. Soc. Chem. Ind.* **49**, 139 (1930)) are of interest: "It is natural to assume that the latent image in the photographic process is made up of metallic silver, which has been split off from the silver bromide by the action of light. That strong light will do this can readily be shown, but the bromine must be separated from the silver as soon as it is formed or else recombination occurs. The bromine is taken up by the gelatine, which acts as an acceptor. Eggert and Noddack have shown that one quantum of light furnishes one atom of silver.

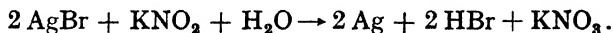
In the phenomenon of sensitization of photographic plates by dye-stuffs, Eggert and Noddack have shown that the dyestuff molecule, itself, is unaltered by this process, and can supply 30 or more silver bromide molecules with the required energy".

Garrison (*J. Amer. Chem. Soc.* **47**, 622 (1925)) has stated that the diamagnetism of silver chloride was reduced and the paramagnetism of silver bromide and iodide increased by exposure of these to radiations from a tungsten filament lamp.

INFLUENCE OF FOREIGN MATTER ON THE BLACKENING OF SILVER HALIDES.

The influence exercised by different substances on the blackening of the silver halides can be divided into groups: (1) The influence is of a catalytic nature and the mechanism is still unknown. Thus Senebier in 1782 observed the marked influence of moisture on the photochemical decomposition of silver chloride. According to the experiments of Spiller (*Z. f. Phot.* 189 (1861)) and those of Baker (*J. Chem. Soc.* **61**, 728 (1892)), carefully dried silver chloride does not blacken in light, but traces of moisture suffice to make it sensitive to light. Cobalt and mercuric chlorides accelerate, whilst chlorides and bromides of the alkali metals retard the blackening.

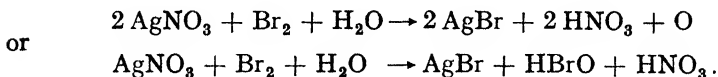
(2) Apart from this catalytic action, there is another reaction of great importance in photography, and this is attributed to the group of coupled reactions. The decomposition of chloride or bromide of silver is facilitated by a series of substances, such as nitrate, citrate and tartrate of silver, sulphites, nitrites, ammonia, gelatin, and other reducing agents, which are capable of absorbing chlorine or bromine. This type of reaction is not catalytic. In presence of gelatin the following reaction is supposed to take place: $\text{AgBr} + \text{gelatin} + \text{light} = \text{Ag} + \text{brominated gelatin}$. Similarly, the reaction in presence of potassium nitrite is as follows:



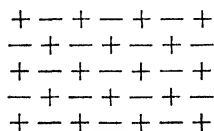
In general, the substance which acts as acceptor does not simply increase the velocity of blackening. It plays the part of extending the light-sensitiveness of the silver halides to longer wavelengths, and this is a special kind of chemical sensitization.

It has been known for a long time that the photosensitiveness of silver chloride or bromide depends a good deal on the conditions in which the salt is precipitated. The light-sensitiveness is increased when the precipitation is effected in presence of an excess of silver nitrate, or any other soluble silver salt, and it is diminished by an excess of KBr or KCl. The influence of soluble silver salts, which is practically utilized in increasing the photosensitiveness of photographic papers, has been

attributed to secondary reactions. It is believed that light first decomposes silver bromide, for example $\text{AgBr} \rightarrow \text{Ag} + \text{Br}$, and that this decomposition is followed by either of the following reactions:

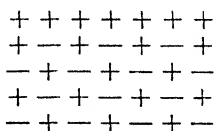


It follows from the researches of Fajans and Frankenburg (*Z. Elektrochem.* **28**, 499 (1922); *Z. physik. Chem.* **97**, 478 (1921)) that, contrary to the mechanism stated above, silver nitrate takes part in the primary process on illumination. They observed that silver bromide, prepared by the action of bromine on solid silver, and then freed from gases in vacuum, and thus free from any adsorbed substances, is sensitive to radiations of wavelengths shorter than 4350 Å. This behaviour is also shown by silver bromide precipitated from excess of bromide ions, and afterwards illuminated in presence of sulphurous acid for the absorption of bromine. When silver bromide was precipitated from excess of silver nitrate, it was sensitive to the whole visible spectrum, including wavelengths longer than 6200 Å (red light). The same sensitivity was observed with silver bromide prepared in presence of an excess of bromide ions, but illuminated in presence of KOH. Fajans and Frankenburg have stated that red light causes the decomposition of only the surface layer of silver bromide. At this stage the silver bromide is no longer sensitive to red light, but is only sensitive to radiations of wavelengths shorter than 5780 Å. Moreover, silver bromide prepared in a vacuum, and sensitive only to radiations of wavelengths shorter than 4350 Å, can be made sensitive to all wavelengths shorter than 5780 Å by an initial illumination with light of wavelengths shorter than 4350 Å. Fajans and Frankenburg explain the increased sensitiveness in the following manner: According to the researches of Wisley (*Phil. Mag.* **42**, 262 (1921)) and Haber (*Ber.* **55**, 1717 (1922)) on the X-ray spectrum of silver bromide, one can conclude that, though silver bromide looks amorphous, it has really a micro-crystalline structure. Each particle of silver bromide is formed of Br ions and Ag arranged regularly as in a crystal of AgBr (Scheme I).



BrAg

(Scheme I)



BrAg + Ag^o

(Scheme II)

In the photochemical decomposition of silver bromide, the primary change is the passage of an electron from a bromide ion to a silver ion. On the other hand, the particles of silver bromide formed in presence of an excess of silver nitrate are charged positively, and the positive charge is due to the adsorption of silver ions, as was first proved by Lottermoser (*Z. physik. Chem.* **60**, 451 (1907); **62**, 359 (1908); **70**, 239 (1910)) (vide scheme II). Now, one can conceive that the energy necessary for the transport of an electron from a bromide ion to a silver ion from the superficial layer formed mainly of positive silver ion, is less than the energy necessary for the removal of an electron from the bromide ion to the silver ion if the superficial layer consists of bromide ions as in the pure salt. The value of the quantum necessary for the decomposition is then diminished by the superficial layer of Ag ions. Hence the increase in the light-sensitiveness due to the presence of silver nitrate is really due to the adsorbed silver ions. Silver bromide blackens in red light in presence of traces of NaOH, NH_4OH , Na_2CO_3 , etc. Fajans and Frankenburger explain this fact on the view that by the action of alkali on AgBr, a small amount of Ag_2O is formed, and that this is highly photosensitive and decomposes readily in radiations of longer wavelengths (red light).

The colour taken up by silver bromide in red light sensitized by silver nitrate or an alkali does not surpass gray. The transformation stops when the adsorbed silver ions or the silver oxide formed disappear.

In order to explain the sensitiveness to light of wavelength 5780 Å of the purified silver bromide prepared in a vacuum after an initial illumination with 4350 Å, Fajans suggested that an adsorption complex $\text{Ag}-\text{AgBr}$, in which the dissociation energy is lowered by the action of adsorbed silver atoms, is formed. Fajans pointed out that although the heat of dissociation of solid silver bromide is 111,000 calories per gram mol, it is decomposed by radiations of wavelength 4350 Å, which correspond to 65,000 calories. It is clear therefore that the heat of adsorption of silver atoms, which is probably more than 30,000 calories, supplies a part of the energy required for the dissociation of silver bromide.

Recently, Masaki (*Japan. J. Phys.* **2**, 163 (1923)) stated that heating photographic plates to 100° photosensitizes them to extremely long light waves. Using ordinary plates and heating them Masaki could go up to 8000 Å, and with panchromatic plates even up to 10,000 Å. The nature of this sensitization is not clear, but it has been observed that it is possible only in presence of gelatin, which is likely to cause a

slight reduction of silver bromide at 100° , so that nuclei are supplied for the photo-sensitization.

J. K. Kier (Z. anorg. Chem. **179**, 89 (1929)) has shown that the alteration of colour exhibited by a thin film of silver iodide, when exposed to light, is due to the production of fine particles of silver. Mut. (Z. phys. Phot. **26**, 193 (1928)) has stated that the bromine liberated by the photolysis of silver bromide in presence of water exists as free bromine. Nitric acid dissolves photolytic silver in small degree. The reaction which takes place in the photolysis of silver bromide appears to be applicable to all silver halides.

Kieser (Z. phys. Phot. **26**, 1, 275 (1928)), darkened silver halide emulsion of colloidal silver in a medium of silver halide. To determine the effect of silver, the photographic layer is washed into a flask and treated with alkaline thiosulphate for 20 minutes in the dark, when the halide dissolves. The precipitate is then collected and ignited wet. The quantum yield for blue light (5000—4000 Å) was determined for different times of exposure to light of 4360 Å, the absorption being calculated from reflexion measurements owing to the thickness of the layer. For short exposures the quantum yield is approximately unity for silver bromide in presence of sodium nitrite, but in water the quantum yield varies from $\frac{1}{15}$ to $\frac{1}{20}$. For longer exposures, the fall of quantum efficiency and the yield of silver decreases to an extent dependent on the form of the precipitate, and thus on its preparation. Kieser (ibid. **26**, 321 (1929)) has also developed a theory to account of the formation of the latent image, based on the quantum theory and the probable alterations in the structure of the silver bromide crystal which accompany photolysis.

Steiner (Z. physik. Chem. **125**, 275 (1927)) has shown that the photo-sensitization of silver bromide in presence of an excess of silver ions takes place also in acid solution, thus excluding the possibility that the sensitization is due to the adsorbed hydroxyl ions. The sensitivity of silver bromide in presence of an excess of bromide ions is the same in neutral and acid solutions with ethylene as acceptor. The behaviour of silver chloride is similar to that of silver bromide. As in the case of silver bromide, silver chloride in presence of an excess of silver ions is sensitized to wavelengths longer than 6150 Å by treatment with sodium carbonate, i.e. hydroxyl ions. Lead ions do not sensitize silver bromide. Thallium ions sensitize silver bromide, in excess of silver ions, to wavelengths greater than 6150 Å.

Steiner and Steiner (ibid. **125**, 307 (1927)) have suggested that the sensitization of silver bromide or chloride is due to the ad-

sorption of ions on the halide lattice. It is reported that the sensitizing effect is due not to the ions functioning as halogen accelerators, but to their direct influence on the primary photochemical change. The effect of anions consists in the formation of an adsorbed layer of the corresponding silver salt, which decomposes in the presence of light of suitable wavelength.

Fajans, Fromherz, and Karagunis (*Z. Elektrochem.* 38, 34 (1927)) have also suggested that there is the possibility that long wavelengths are absorbed by silver bromide, containing an excess of bromide ion, to the same extent as silver bromide containing an excess of silver ion, but that the red rays are active only in the latter case, because the reaction with the excess of the silver salt binds the bromine and prevents back reaction. To test this point, the influence of adsorbed ions on the light absorption of silver bromide was studied. Sols containing about 1 millimol of silver bromide per litre were prepared with excess of silver nitrate or of potassium bromide, varying from 0 to 1 millimol per litre. The degree of coagulation of these sols became stationary after 12 hours. During the next two hours, which was the time necessary to carry out measurements of absorption, it did not vary more than 1—2%. The dispersity of a sol containing 100% excess of silver nitrate was the same as that of the sol containing 5% excess of potassium bromide. These two sols were used for the purpose of absorption measurements. Silver bromide-gelatin emulsions were also studied. With aqueous sols, the extinction coefficient is practically the same for both sols in the region 3800—4470 Å. It appears that scattering is largely responsible for the light extinction. There is a marked difference between the extinction of silver bromide containing an excess of silver salt, that of silver bromide containing an excess of bromide ion, and that of pure silver bromide. The extinction coefficient of silver bromide in presence of an excess of silver ion even in the near ultra-violet is greater than that of the silver bromide containing an excess of bromide ion. Hence the absorption of light by silver bromide is influenced by adsorbed ions. The difference between the extinction coefficients of silver bromide containing an excess of silver ion and of silver bromide containing an excess of bromide ion, increases, passing from the ultra-violet to the yellow, with both plates and sols. This indicates an extension of the light absorption into the longer wavelengths by the adsorbed silver ions. It is assumed that the energy of the absorbed light quantum depends only on the absorption energy in the first phase of the process of transfer of an electron from a bromide to a silver ion, i.e. on the separation of an electron

bromide ions will therefore, depend on the condition of the bromide ions in the silver bromide space-lattice. It is also markedly different in the case of sodium bromide from that of silver bromide, owing to the deforming action of the silver ions on the bromide ions, on the surface of silver bromide. The shift of absorption due to adsorbed silver ions is caused by their distorting effect on the neighbouring bromide ions in the silver bromide lattice.

Recently Fajans and Karagunis (*Naturwiss.* **17**, 274 (1929)) have shown that when Ag^+ and Tl^+ ions are adsorbed by colloidal silver bromide or Pb^{2+} ions by lead iodide, the strongly anion-deforming cations bring about an increased light extinction, detectable on the long wavelength portion of the absorption curve. Silver iodide, so highly transparent that scattered radiation plays a minor part, permits the measurement of intensities on both sides of the absorption maximum at 4200 Å. Adsorption of Ag^+ ions in this case causes the intensity of the whole band to be increased markedly, without appreciable shift of the wavelength of maximum absorption. The adsorption of Ag^+ on the silver iodide lattice increases either the number of atoms in the particular state, or the number of quantum transitions, of which the band forms a measure. The transition is probably in the photoelectric conductive state and the photodecomposition of the silver halide.

Kobayashi (*Naturwiss.* **16**, 530 (1928)) has exposed gelatin-free silver chloride to monochromatic light of wavelength 3650 Å, under such conditions that the whole of the incident light was absorbed. The halide was immersed in water, so that the liberated chlorine would appear as hydrochloric acid and hypochlorous acid. Analysis of the solution indicated that the ratio chlorine atoms/quanta is 0.86. The slight variation from Einstein's law of equivalence is ascribed to light absorbed by silver formed in the photochemical reaction.

Hofstad and Schmidt (*Z. Physik.* **48**, 541 (1928)) have measured the absorption spectra of thin sheets of microcrystalline silver bromide and silver chloride, photographically. The converging frequencies in the long wavelength region were found to be 4800 Å for silver bromide, and 4000 Å for silver chloride. The small amount of silver liberated from the bromide under the action of light caused no perceptible change in the absorption spectrum.

See also *Nature* Sept. 24, 1927; compare *Phil. Mag.* **3**, 482 (1927)) to make a distinction between photoelectric and photo-conductive properties of silver halides; the former consists in the complete liberation of the electrons, and the latter in the freeing of electrons partially, resulting in a change in conductivity. Since the photographic

action in a bromide emulsion takes place with a wavelength much longer than the longest capable of producing photochemical emission from silver bromide, the photographic mechanism does not appear to be photoelectric.

The influence of light of different wavelengths is roughly parallel for the photographic and photo-conductivity effects. Thus, a slow silver bromide emulsion shows zero sensitivity at wavelengths greater than 5000 Å, and Coblenz has shown that the photo-conductivity becomes measurable with light of the same wavelength. Both the photographic and photo-conductivity effects are increasingly strongly exhibited as the wavelength decreases, and very likely these effects are identical. Hence it would appear that the formation of the latent image involves the transfer of valency electrons from bromide ions to silver ions, resulting in the formation of metallic silver atoms. Recently, Toy and Harrison (*Nature* **123**, 579 (1929)) have shown that the photo-current due to liberated valency electrons that pass through a thin layer of silver bromide fused between two electrodes, starts instantaneously on illumination, and quickly reaches a steady value. Sheppard (*Nature* **123**, 979 (1929)) has stated that the results of Toy and Harrison (*loc. cit.*) support the view that the photoelectric effects (photo-voltaic and photo-conductivity) and the photographic and photochemical effects, are all derived from the primary separation of the electron from the bromide ion. It appears that the formation of a latent image involves both the segregation of silver and the aggregation of the silver atoms produced.

According to Sheppard, Trivelli, and Loveland (*J. Chem. Phys.* **200**, 51 (1925)), the main function of the specks of sensitizing silver sulphide, telluride, and selenide, is to collect about themselves silver atoms produced in the photochemical decomposition of silver bromide, so that ultimately a developable aggregate is formed. It is highly probable that the silver nucleus must exceed a certain minimum size. It has been claimed by the above authors that the use of any of the following compounds enables ordinary gelatin to be converted into active gelatin, and causes the ripening steps in the preparation of emulsions to be dispensed with wholly or in part: thiocarbonyl (aryl, acyl), thiocarbamides, allyl isothiocyanate, phenylthiocarbonyl, phenylthiocarbamide, thiosemicarbazide, sodium thioacetate, ortho-tolyl thiocarbamide, etc. These views of Sheppard, Trivelli, and Loveland have been confirmed by other workers.

Feick and Schaum (*Z. wiss. Phot.* **23**, 398 (1925)) have determined the dielectric constants of thalious chloride, silver chloride, and silver

with increased exposure to light. In the case of silver exposures gave no measurable effect.

Reiss (*Z. Physik.* **32**, 38 (1925)) have shown that when halides, prepared in a variety of ways, are suspended in an electric field between the plates of a condenser and are illuminated by a point-o-lite lamp, silver bromide loses 25% of its bromide less, and silver iodide shows no loss at all.

Volger (*Ann. Physik.* **77**, 495 (1925)) have pointed out that if the formation of a latent image is due to the passage of an electron to the bromide ion to the silver ion with consequent separation of the crystal lattice of the silver bromide should suffer deformation. This view has been tested by the Debye-Scherrer method. The X-ray spectrum of the darkened halide showed that the rings due to silver are superimposed on the bromide rings; thus the evidence of the formation of a subhalide. From the evidence it appears that the conception of a silver halide adsorption gives the true picture of a photohalide.

Silberstein (*Phil. Mag.* (VII) **5**, 464 (1928)) has pointed out that to modify the quantum theory of photographic exposures adequately (ibid. (VI) **44**, 257 (1922), (VI) **45**, 1062 (1923)) have led to unsatisfactory results. Similarly, the assumption of Toy (*Trans. Faraday Soc.* **19**, 209 (1923)) that prior to the exposure there are a certain number of nuclei distributed haphazardly amongst the grains of the emulsion, so that the energy required to convert them into latent centres is a Maxwell distribution function, does not represent the experimental data. Silberstein has now developed a theory based on the "concentration speck" theory of Sheppard, Trivelli, and Loye (*J. Franklin Inst.* **200**, 51 (1925)), in which the rate of increase of area of a nucleus is considered to be proportional to the original area, and quantum relationships are assumed. Values calculated from the theory are in agreement with the results observed for several emulsions (compare Sheppard, *Nature* **121**, 574 (1928)).

Adit and Pretschner (*Z. wiss. Phot.* **27**, 36, 173 (1929)) have observed that the highly dispersed portion of silver in photographic emulsion is removed by treating it with dichromate and sulphuric acid. Sensitivity is probably affected by the deposition of some silver ions. Sodium sulphite has been found by the above authors to be the most satisfactory fixing agent, as it does not dissolve the silver particles, and, the complexes formed with silver halides being easily washed out of the gelatin film.

Recently, Ram Behari Lal and Dhar have shown that the reduction of silver chloride, silver bromide, silver iodide, and silver thiocyanate by reducing agents like pyrogallol, hydroquinone, hydrazine hydrochloride, hydroxylamine hydrochloride, etc., is increased by the addition of sodium sulphite. The greater the amount of sulphite, the greater is the reduction of the silver salt with a definite amount of the other reducing agent.

In the case of silver iodide Lüppo-Cramer (Z. phys. Chem. 11, 1 (1929)) observed solarization before the maximum possible sensitization occurred. Thallous iodide increases the sensitivity of silver iodide in much the same way as silver bromide.

It will be evident from the foregoing pages that there is a wide scope for research work in the different branches of photographic chemistry.

PRINCIPLES OF PHOTOGRAPHIC PROCESSING

A veritable photographic process was realized by Nicéphore Niépce and Victor about 1825. The photosensitive substance was bitumen of soda, which is transformed by oxidation in light, and is rendered insoluble in organic solvents. This property is still utilized in the photochemical reproduction of images. For ordinary photography, however, the sensitiveness of bitumen is insufficient.

(The first photographic method which has been truly successful is due to Daguerre (1838). The obtaining of a daguerreotype requires the following operations: A polished piece of silver is first subjected to the action of iodine vapours in the dark, and thus the surface is covered by a thin layer of silver iodide. It is then exposed in a dark room according to the usual procedure. The light does not produce any visible effect, but only a *latent image*, which becomes apparent when the plate is exposed to the action of mercury vapour, which condenses solely on the illuminated parts, and forms with silver an amalgam. The light is not equally reflected by the amalgamated surface and that which is not amalgamated, and if the plate is viewed at an inconvenient angle an image of the object is seen. This image can be fixed by a solution of sodium thiosulphate.)

The Daguerre process is rather an inconvenient one, and has been replaced by the Talbot process, in which a paper impregnated with a silver salt is dipped into a solution of a redoxing agent under illumination. An image is formed, in which light and shade, in comparison with the object, appear to be reversed. This negative is used for obtaining as many positive images as are desired.

Victor improved this process by the addition of silver salt to albumin; later on, Fry and Scott Archer replaced albumin by collodion. A solution of collodion is added to an alcoholic solution of CdI_2 and NH_4Br (or CdI_2 and NH_4I), and the mixture is then spread out on a glass plate, which is dipped into a solution of silver nitrate. AgBr or AgI is formed in the collodion. In the wet process the plate should not be prepared a long time in advance, because its sensitiveness decreases when it is dried. The dry plate can, however, be employed if it is sensitized by albumin or tannin (dry process). In these two collodion processes, the developing is done in the usual manner by means of pyrogallol, ferrous sulphate, etc., and the plate is fixed in a thiosulphate bath.

Nowadays, in ordinary photography, gelatin-silver bromide plates—first introduced by Maddox in 1871—are used. The light-sensitive emulsion is obtained by mixing in the dark or in red light, solutions of KBr and AgNO_3 containing gelatin. The silver bromide formed is not obtained as a precipitate but as a milky emulsion, which on cooling becomes a jelly; this is washed to free it from soluble salts, and then melted at a gentle heat and spread out in thin layers on glass plates, or on paper or celluloid. The sensitiveness of the emulsion is increased by maintaining it for a long time at a temperature of about 40° , or heating it for a few minutes to 100° . This operation which is called “ripening” has largely contributed to the success of the gelatin-silver bromide plate. It is of the greatest importance for a latent image, which can be developed, to be formed, even when the exposure is for a short time. Up to the present, only with silver salts, have sufficiently sensitive plates been prepared. In fact, the photochemical yield in the decomposition of silver bromide mixed with gelatin is not high, but a very small photochemical effect suffices for the production of a latent image. The duration of the exposure has not the same importance in the making of a positive image, and many photosensitive substances have been utilized for this operation.

THE LATENT IMAGE AND ITS PHOTOGRAPHIC DEVELOPMENT.

(Numerous hypotheses have been proposed regarding the nature of the latent image. Certain authors have attributed its formation to an alteration which is simply of a mechanical or physical nature, such as the passage of the silver bromide from the colloidal to the crystalline condition, or a change in the cohesion of the silver bromide

molecules. This view seems to be justified for the daguerreotype photographic plate. Light produces a change of structure of silver iodide, and it is known that vapours condense more readily on a rough surface than on a polished one. It seems probable, however, that a change of structure is not directly produced by light, but that it is a secondary effect of chemical transformation. It appears certain that in the ordinary plate change of structure does not intervene in the formation of the latent image, or only plays an accessory rôle. It has been known for a long time that a plate can be developed after a primary fixing. Sodium thiosulphate does not dissolve the substance of which the latent image consists, and it appears that there exists a form of silver bromide insoluble in sodium thiosulphate.)

(Nowadays, the physical theories have been abandoned by everybody, but there is difference of opinion regarding the nature of the chemical transformation undergone by silver bromide on illumination. Although there is no doubt that the blackening results from the liberation of metallic silver, it appears natural to suppose that the formation of ultramicroscopic germs of silver occurs in the invisible impression produced during the short photographic exposure. This seems to be the opinion of the majority of photochemists. However, there are others, such as Volmer and Schaum (*Z. wiss. Phot.* **14**, 1 (1915)), who suppose the formation of free silver in the intense blackening, but advocate the hypothesis of the formation of a subhalide in the latent image. The principal argument in favour of this view is furnished by the resistance of the latent image to oxidizing agents.) As a matter of fact, several oxidizing agents such as chromic acid, permanganic acid, halogens, etc., destroy the latent image. According to Eder, a mixture of chromic and nitric acids is particularly active, but dilute nitric acid is without action, and strong nitric acid acts but slowly. (Lüppo-Cramer has observed that the image is much less resistant in the emulsions with fine grains than with emulsions of large grains.) The latent image is easily destroyed by solutions capable of dissolving both metallic silver and silver bromide (e.g. HNO_3 and NH_4CNS).

The comparative stability of the latent image towards oxidizing agents is, however, not incompatible with the hypothesis of germs or nuclei of silver. It is known that colloidal mixtures sometimes yield unexpected results. Thus Lüppo-Cramer has stated that from a mixture of hydro-sols of silver and silver bromide, the metal is dissolved by nitric acid if this is added immediately after mixing colloidal

silver and silver bromide. If the colloids are first coagulated by the addition of sulphuric acid, it becomes impossible to extract the silver by nitric acid. It appears certain that light has the effect, even after a short exposure, of liberating metallic silver, which remains adsorbed by the silver bromide, and the silver is therefore not readily attacked by the oxidizing agents. The development of a photographic plate can be made after a primary fixing by a bath of sodium thiosulphate. It is necessary to have recourse to solutions containing silver nitrate and a reducing agent, such as pyrogallol; and these solutions decompose slowly and deposit silver on those parts of the plate which have been affected by light. We have here a phenomenon of metallic catalysis. The separation of metallic silver takes place only on the particles of silver which consist of the latent image and act as centres of crystallization. Their action is similar to those of crystalline germs, which cause the release of a supersaturated solution.)

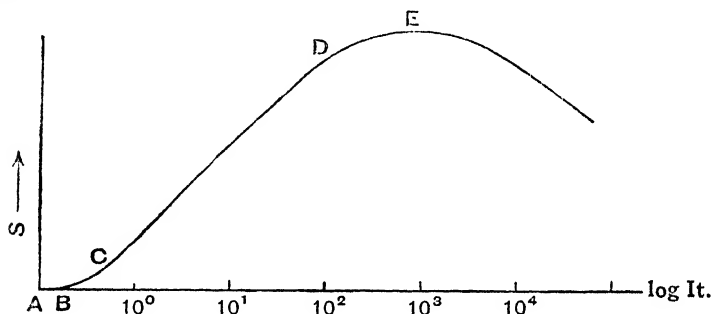
INFLUENCE OF DIFFERENT FACTORS WHICH INTERVENE IN THE FORMATION OF THE LATENT IMAGE.

The effect of light in the process of photography can be expressed by the quantity of silver liberated by a unit surface. It is, however, not easy to measure directly this quantity. In practice this quantity is measured optically.

The name *opacity* has been given to the ratio $\frac{I_0}{I}$ between the intensity of the incident light and that of the light transmitted by the plate. The degree of blackening is the logarithm of opacity. If S represents the blackening, then we have the relation $S = \log \frac{I_0}{I}$. From the point of view of practical photography, it is the blackening or the opacity which is the interesting thing, but this is really a measure of the quantity of silver deposited, provided the plates which are compared have the same structure and contain grains of silver of the same size. The blackening depends on numerous factors. First of all, it is a function of the impression produced by light, and consequently depends on all the influences which intervene in the formation of latent image, intensity, wavelength of the light, duration of the exposure, temperature, and sensitiveness of the plate. It depends also on the development, its duration, and the composition and temperature of the developing bath.

INFLUENCE OF THE QUANTITY OF LIGHT.

The blackening after development does not increase, as is expected, proportionally to the product (It) of the intensity and the duration of the exposure, which is measured by the quantity of light received by the plate. If degrees of blackening are plotted as ordinates and logarithms of the quantities of light as abscissae, with the ordinary photographic plate, a curve of the type given is obtained:



In the curve there is a period of induction AB , in which light has no appreciable effect. For obtaining a latent image which can be developed, it is necessary to pass the *threshold value* B , which corresponds for ordinary rapid plates to the value 0.1 candle power (per metre per second). Then comes a period of *subexposure* BC , during which S increases nearly proportionally to It . Then there is the period of *normal exposure* CD , corresponding to a nearly rectilinear part of the curve ($S = c \log It$), and finally there is the period of *over exposure*, in which S increases more and more slowly, reaches a maximum, and then decreases. When the maximum is passed, *solarization* takes place. The phenomenon is observed easily when a highly luminous object is photographed, such as the sun surrounded by clouds. Those parts of the plate, which have been most strongly illuminated, blacken less than the other parts in the development, and in place of a negative a positive is obtained.

In the ordinary plates, the inversion E is produced when the amount of light is of the order of 1000 candle power (per metre per second), but the solarization is retarded by chemical sensitizers, such as sodium nitrite. In plates, of which the sensitiveness for a normal exposure had been rendered 2 to 4 times greater by these substances, Eder has stated that the quantity of light necessary for producing

solarization becomes 5 to 50 times more elevated. The solarization becomes less, or is suppressed, when the overexposed plate is treated with a bromine solution (Volmar and Schaum) or other oxidizing agent such as HNO_3 and $\text{H}_2\text{Cr}_2\text{O}_7$ (Eder, Lüppo-Cramer). It is also decreased by a bath of thiosulphate, and Lüppo-Cramer has obtained normal images by development after fixing the ordinary plates, which have been solarized.

When the exposure is of a very long duration, and the light source is highly intense, the phenomenon becomes more complicated. There is a second and sometimes a third inversion. These multiple inversions were first observed by Janssen (*Compt. rend.* **91**, 119 (1880)) in photographing the sun (1880). They have also been observed by Guebhard (*Rev. d. Sc. Photogr.* **2**, 161 (1905)), and by Bouasse (*Ann. de la Fac. de Sc. de Toulouse* **8**, 26 (1895)). Numerous explanations based on the hypothesis of the formation of subhalides have been advanced in explaining the phenomenon of solarization. Scheffers (*Z. Physik.* **20**, 109 (1923)) and d'Arens (*Z. physik. Chem.* **114**, 337 (1925)) have studied the problem from various points of view, and have advanced the hypothesis that solarization is caused by the coagulation of the silver germs. Their experiments show that in the action of light on an over-exposed plate, there is an increase in the amount of free silver, and also that under certain conditions the particles of colloidal silver do not act as nuclei for development. Scheffers has stated that the velocity of development of silver sols when the size of the particles is varied resembles what occurs in the phenomenon of solarization. It can be imagined that in the action of light on a photosensitive emulsion, there is the formation of finely divided silver, which acts as a catalyst in the development. If the illumination is prolonged, these particles increase in number, and later on they become larger and inactive. This view enables us to understand how solutions of oxidizing agents, which dissolve silver, suppress solarization.

In the ordinary photographic plate, the photosensitive layer contains a large number of grains of AgBr at different depths. When the plate is illuminated, the phenomena of dispersion, refraction, and absorption complicate the investigations of the effects produced by light. Svedberg (*Colloid Chemistry* p. 68 (1924)) has avoided this inconvenience by using plates with very thin layers, in which the grains appear distinct from each other in the microscope. The microphotographs of these plates taken in red light, (a) before development, (b) after development, (c) after development and dissolution of the free silver by a solution of potassium permanganate or dichromate

show that, as a rule, the grains attacked by the reducing agents (developers) are completely reduced. After treatment by a solution which dissolves silver, no trace of silver is left in the layer. However, the reduction is not complete if the developing bath contains an appreciable amount of KBr, which retards the development. Also, the reduction of a grain, which has been acted upon by light, does not lead to the reduction of a neighbouring grain. Hence the grain of silver bromide is a unit in the phenomenon of photography. Svedberg has exposed the plates during different intervals of time to diverse light radiations, α -rays, β -rays, and X-rays. By a laborious process of actual counting, the percentage of grains rendered developable has been determined in each case. This percentage P has not been taken solely on the total number of grains, but it has been determined partly for a group of grains of the neighbouring dimensions. With X-rays, the results are relatively simple. Mühlestein (*Arch. Sc. phys. et nat. Genève V* 4, 38 (1922)) has stated that each grain which is encountered by one of these particles is rendered developable. Svedberg came to the same conclusion indirectly. If k represents the number of α -particles which meet the photographic plate per second, and in an area equal to the apparent surface of a grain, the probability of each grain to be met by at least one α -particle after t seconds is equal to $1 - e^{-kt}$, and for 100 grains we get $P = 100(1 - e^{-kt})$. According to Svedberg, this formula expresses very well the variations of the percentage of developable grains as a function of kt .

With β -particles an analogous curve was obtained, but it appears that several β -particles are taken up by the grain before it can be developable.

For light radiations, the curve of variations of P as a function of time has another form. It presents an evident analogy with that of the blackening before the first inversion point already discussed.

Svedberg has tried to show that there are developable centres in photographic plates which have been acted upon by light, and attempted to establish the law of their distribution amongst the silver bromide grains. The method of observation was as follows:

A photographic plate, which has been acted upon by light, is developed for a short time (15 seconds) by a suitable developer. A microphotograph in red light does not show any change of grains. Now the plate is fixed by a solution of thiosulphate. A new microphotograph makes visible the black points which are found exclusively on the sides first occupied by the grains. Statistical study of their distribution in the central part and on the edges of the grain led

Svedberg to the conclusion that the black points are localized in the superficial layer of the grains. These points are the centres from which the reduction of silver bromide takes place. During their development, their dimensions increase to such an extent that the grain is totally reduced to metallic silver. If, in a plate, the mean number of centres per grain is equal to v , the probability of a grain containing at least one of these centres is equal to $1 - e^{-v}$, and for 100 grains, we get the relation

$$P = 100 (1 - e^{-v}).$$

The determination of the values of P and v has permitted Svedberg to verify this relation. The sensitiveness of a plate is in close relation with the number of developable centres formed on a unit surface in a given exposure. The measurements of Svedberg have shown that in the same emulsion, prepared with certain precautions, the mean number of centres per grain increases proportionally to the surface of the grain. When one passes from one plate to another, the number of centres per unit surface varies considerably, and in the same emulsion the grains are only comparable when they are formed under the same conditions. For explaining these observed facts, Svedberg has proposed the following hypothesis: The developable centres can be formed on all the surface of the bromide grains, but the sensitiveness varies from point to point of the surface. The energy of the α -particles is sufficient for producing a developable centre, whatever may be the point where the α -particle meets the grain. The energy of the β -particle is equally sufficient, but these particles do not always give up enough energy to the surface of the grain. The result is that the number of grains rendered developable increases according to the exponential formula discussed before. The energy of the light quantum, on the contrary, is too feeble for producing a centre. In order that a grain may become developable, it is necessary that a certain number of quanta should be absorbed in a given area of the surface of the grain. The experiments carried out in the Eastman Kodak Laboratory seem to indicate that the number of quanta required goes up to several hundreds. This fact supports the view that the particles of silver should attain certain dimensions in order to act as developable centres. This supposition is rendered probable by the observations of Zsigmondy, according to which the particles of colloidal gold act as nuclei in the reduction of a gold salt only when they have a certain size. Similarly, the effect of light on a photographic plate becomes appreciable only when the exposure is of a certain minimum duration.

In the above considerations, we have assumed implicitly that the formation of a latent image under certain experimental conditions, is determined by the quantity of light received by the plate. The experiments of Bunsen and Roscoe (*Pogg. Ann.* **117**, 576 (1862)) on the blackening of silver chloride, led these savants to the conclusion that the photochemical effect remains constant, when I and t are varied in an inverse ratio so that their product becomes constant. We know that this relation holds good in a large number of photochemical reactions. However, this relation is not exactly applicable to the action of light on silver salts. In 1844, Fizeau and Foucault (*Compt. rend.* **18**, 746 (1844)) stated that the effect produced on a Daguerre plate by a given quantity of light decreases when the light intensity becomes less than a certain limiting value. This phenomenon was first observed by Miethe (*Thesis*, Göttingen (1889)) in a gelatino-bromide plate, and has also been observed by other workers. Abney (*Eder's Jahrbuch* **123**, 139, 174 (1895)) obtained the following relations for the same quantity of light:

(1) A long exposure with light of very feeble intensity produces less effect than that produced by more intense light lasting for a short time.

(2) At constant intensity, the total effect of n successive exposures of short duration t/n is less than that of one exposure lasting for time t . These results have been confirmed by Englisch, Schwarzschild, Odenrantz, and others. According to Schwarzschild, the photochemical effect is a function not of It , but of Iqt , where q is nearly constant for a given kind of plate. These phenomena seem to indicate a reversibility in the action produced by light. Regarding the nature of the reversible phenomenon, there is difference of opinion. It is probable that a chemical change takes place, in which bromine intervenes. Now the deviations from the law of Bunsen and Roscoe are only slight, and sometimes hardly observable in rapid emulsions impregnated with substances capable of uniting with bromine. It seems also that the phenomenon is produced in plates which have been slightly affected by light; and it is observed immediately after the action of light. In a plate which has been normally affected by light the latent image develops only very slowly.

VILLARD, CLAYDEN, AND HERSCHEL EFFECTS.

The impression produced by X-rays on a photographic plate is partially destroyed by a subsequent prolonged action of light. This phenomenon is known under the name of Villard effect. In the Clayden

effect the latent image produced by electric sparks is diminished by white light. Finally, the Herschel effect consists in the weakening of the impression produced by white light on certain plates containing an excess of KBr by the subsequent action of red light. None of these effects is observed if the order of the two successive actions is reversed. For example, the latent image produced by ordinary white light is not affected by X-rays or electric sparks. According to the researches of d'Arens, the Villard and Clayden effects are due to the same cause as solarization. X-rays lead to the formation of very small silver particles at the surface of the bromide grains. These small silver particles are very active in the development. The light which acts subsequently gives rise to larger particles, which absorb the fine particles first formed, and thus the catalytic activity is diminished. The Herschel effect is undoubtedly due to another cause. Arens attributes it to the oxidation of silver by bromine.

INFLUENCE OF TEMPERATURE ON PHOTOGRAPHY.

The formation of the latent image, like several other photochemical changes, is only feebly influenced by temperature. Dewar (*Chem. News* **84**, 281, 293 (1901)) observed that even at -252° , light produces an impression which is developable. The sensitiveness of the plate at this low temperature is about $\frac{1}{10}$ of that at the ordinary temperature. According to the measurements of Padoa and Mervini (*Atti R. Accad. Lincei*, **25**, 168 (1916)), the temperature coefficient of the formation of the latent image is 1.05 between 15° to -85° , and is independent of the wavelength. Similar results have been obtained by Dalezki and Plotnikoff (*Lehrb. d. Photochemie*, 71 (1920)).

In the direct blackening of silver citrate paper, the influence of temperature is slightly more pronounced, and depends on the wavelength; and Padoa and Mervini obtained 1.07 as the temperature coefficient for ultra-violet rays, and 1.19 for blue rays. The velocity of development, however, is highly influenced by temperature. The action of hydroquinone, for example, is practically stopped at 0° , and at higher temperature there is not only acceleration of the development but the silver bromide which has been unaffected by light is also reduced and the plate becomes foggy.

FACTORS WHICH EXERT AN INFLUENCE ON THE SENSITIVENESS OF PHOTOGRAPHIC PLATES.

① First, size of the grains.—It has been known for a long time that the size of the grains has a great influence on their sensitiveness.

In general, emulsions with fine grains are less sensitive. The plates employed in colour photography according to the Lippmann method, of which the grains have diameters between 0.1 to 0.3μ , are about 30,000 times less sensitive than rapid plates, which contain grains having diameters of the order 2 to 3μ . Moreover, the process of ripening (maturing) leads to increase of the sensitiveness and of the size of the grains.

It seems probable, however, that the great variations of the sensitiveness are not due to the dimensions of the grains, of which the rôle has been exaggerated. The researches of Koch and Prel (*Physik. Z.* **17**, 535 (1916)) have led to the conclusion that there is no relation between the sensitiveness of the grains and their size. Similar results have been obtained by Svedberg, who showed that the number of developable centres in the grains of the same emulsion increases proportionally with the surface of the grains. The sensitiveness per unit surface is the same for the small as well as the large grains. If, on the contrary, emulsions prepared under different conditions are used, the number of centres formed in a unit surface of the grains varies considerably.

CHEMICAL SENSITIZERS.

The sensitiveness of gelatino-bromide plates is increased by the presence of small quantities of silver iodide, or AgNO_3 , KNO_3 , tannin, etc., capable of absorbing bromine. The mode of action of sensitizers has already been discussed. According to Lüppo-Cramer (*Photogr. Problem.* **41** (1907)), their influence is only manifested in the direct blackening, and not in the formation of the latent image. It is a well known fact that the relative sensitiveness to direct blackening, and that related to the impression to be detected only by development, do not vary in the same proportion. Thus plates with very fine grains blacken more quickly than rapid plates, which, however, blacken much less readily than silver chloride paper, which, in its turn, is slightly sensitive to the formation of the latent image. The gelatin exerts a certain amount of influence on the sensitiveness of the plate. The majority of authors believe that it acts as an acceptor of bromine. The view has been expressed that gelatin is adsorbed by silver bromide during its precipitation, and that variations of the sensitiveness depending on the mode of preparation of the emulsion depend to a large extent on the difference of this adsorption of the gelatin.

OPTICAL SENSITIZERS.

The sensitiveness of an ordinary plate is at a maximum in the blue and remains marked up to extreme ultra-violet. Towards the side of longer wavelengths it diminishes rapidly, and the yellow rays are entirely without action. This unequal sensitiveness to different colours is a matter of great inconvenience. The relative visibility to the naked eye of different colours is very different from photographic sensitiveness. Thus, the yellow colour, which strongly affects the eye, gives black in the positive, whilst the violet gives a light effect. This defect of ordinary plates can be corrected by optical sensitizers. As early as 1873 Vogel (*Ber.* 6, 1305 (1873)) stated that an emulsion of collodion and silver bromide containing certain colouring matters becomes sensitive to the rays absorbed by the colouring matters. We have already seen that this is the first case of optical sensitization to be observed. Vogel's discovery bore fruit in panchromatic and orthochromatic photography. In general, the maximum of sensitiveness corresponds to a maximum of absorption. Not all coloured substances are active. In order that a coloured substance may be active, it is necessary for it to be adsorbed by the bromide, or, in other words, it should colour the bromide. It seems probable, also, that the colouring matter, which acts as an optical sensitizer, should have a certain amount of photochemical sensitiveness. Amongst the substances possessing optical sensitizing power, the following may be mentioned:

For the greenish blue: chrysaniline, acridine yellow, uranine.

For the yellowish green: eosin, erythrosin, quinoline red.

For the orange: cyanine, methylviolet.

For the orange red: nigrosine, pinacyanol.

For the red and infra-red: dicyanin, neocyanin.

All these substances have not the same practical importance. In order that the different colours may produce the impressions corresponding to their visibility, it is necessary that the sensitiveness to the yellow and green radiations, to which the eye is very sensitive, should be increased. Eosin and erythrosin, which show the maximum of absorption in the yellow green part of the spectrum, are very convenient for the purpose of sensitization to visible light. Cyanine, which absorbs specially in the orange, increases the sensitiveness to red light better than eosin; but it has a tendency to fog the plates, and it is seldom used without mixing it with other sensitizers.

For colour photography by the Lumière process, it is necessary that the emulsion should have as uniform a sensitiveness as possible

to all parts of the spectrum. Panchromatic plates can be obtained by sensitizing the ordinary plates with orthochrome *T* or ethyl red, which possess two maxima of absorption, one in the green and the other in the yellow.

Ethyl red (isocyanine) has been used for sensitizing to orange light. The blue lepidine cyanines extend the sensitivity into the red. Orthochrome *T* (p-toluquinaldine-p-toluquinoline-ethyl cyanine) gives a very uniform sensitization, whilst pinachrome (p-ethoxy quinaldine p-ethoxyquinoline ethyl cyanine) sensitises up to 6500 Å. Pinaverdol (p-toluquinaldinequinoline methyl cyanine) is particularly effective in the green and yellow. True panchromatic sensitivity is obtainable with pinacyanol and ethyl cyanine, both being effective to 6800 Å, and dicyanine and neocyanin are useful right up to the extreme limit of visible red and near the infra-red, without causing undue predominance at the other end of the visible spectrum. "Homocol" and "isocol" produced by the Baeyer company are of this type. Kryptocyanine acts as a good sensitizer for the near infra-red rays. It is efficacious up to 8500 Å, and dicyanine even beyond 9000 Å. The nature of the cyanine dyes has been investigated by Mills and collaborators (*J. Chem. Soc.* **121**, 1946 (1922)). Recently Germann and Shen (*J. Phys. Chem.* **33**, 864 (1929)) have discussed different photographic sensitizers.

The optical sensitization of photographic plates has not yet received a satisfactory and precise explanation. It has been suggested that the sensitizer activated by light reacts chemically with the substances contained in the system, but is re-formed by a subsequent reaction. The tendency of certain colouring matters, such as cyanine, to fog the plates shows that they sometimes reduce the silver bromide even in the dark, and that this reduction is accelerated by the light. The view has been expressed by Weigert (*Die chemischen Wirkungen des Lichts* p. 250 (1911)) that the colouring matter simply reacts with silver bromide without being re-formed subsequently. This would not be true optical sensitization, but a simple photochemical reaction between a photosensitive substance and silver bromide. The quantity of colouring matter necessary for the liberation of silver, which forms the latent image, is so small that the disappearance of this amount is likely to remain unperceived. In certain cases, however, the colouring matters act as true photosensitizers and do not undergo any chemical change. It is quite possible as well that the action of the sensitizer on silver bromide is not direct. Several authors have observed that light alters gelatin and renders it less soluble. Meisling has stated that formaldehyde, which renders gelatin insoluble, is formed when

gelatin is exposed to light. Now, the photosensitizers are assumed to favour this transformation of gelatin. Formaldehyde also appears to intervene in the action of gelatin on silver bromide.

We have already seen how the sensitizing action of free silver is explained by Weigert. According to Eder, this metal is an excellent panchromatic sensitizer. The well known fact that a preliminary impression by white light makes an ordinary gelatino-bromide plate sensitive to red or yellow light, should be attributed to the excellent panchromatic sensitizing power of metallic silver. According to Guebard, the increase of the sensitiveness during ripening is probably at least partly due to the partial reduction of the silver bromide by gelatin with the formation of nuclei of silver. Some authors, for example Abegg (*Arch. wiss. Phot.* 1, 15 (1899)), have expressed the view that this reducing action manifests itself even at the ordinary temperature, and thus explains the phenomenon of *autosensitization*, which is the spontaneous increase of the sensitiveness of plates kept in the dark.

OPTICAL DESENSITIZERS AND ULTRA-VIOLET LIGHT PHOTOGRAPHY.

The normal range of sensitivity for an ordinary plate is from 5000 to 2200 Å. Kodak "infra-red sensitive" plates give good results with short exposures up to 11,000 Å. An ordinary tungsten filament lamp or a point-o-lite lamp has a satisfactory intensity up to 9000 Å, and for work above 10,000 Å, a high intensity arc is necessary.

Increased spectral sensitivity, and the approach to true panchromatism, cause difficulties of dark room manipulation. The ruby light, which is useful in avoiding the fogging of ordinary plates, is too bright for orthochromatic plates, and useless for panchromatic plates. Coloured glass cannot be used for dark room illumination, and dyed films of gelatin, or sheets of coloured paper mounted between glass plates, were chosen so as to give a very feeble glimmer of red or green light; but even with these feeble illuminations, a good panchromatic plate is easily fogged. Absolute darkness seems essential for completely avoiding fogging. The problem of dark room manipulation has been solved in another manner. The dyestuff phenosafranine has been utilized by Lüppo-Cramer in decreasing the sensitivity of the exposed plate without destroying the latent image, and in presence of this substance panchromatic plates can be developed in bright yellow light. Phenosafranine desensitizes the plate against

red and violet rays, although it transmits these wavelengths freely. Lüppo-Cramer further showed that the desensitizing action may be specific for one or other of the silver halides, for example erythrosin, pinacyanol, and pinachrome desensitize silver iodide gelatin plates, although they are used as sensitizing agents for silver chloride and silver bromide emulsions. A. and L. Lumière and Seyewetz (*Bull. Soc. chim.* (4) **29**, 565 (1921)) have investigated the relationship between chemical constitution and desensitizing action, and have also shown that phenosafranine does not form a permanent compound with either silver halide or gelatin, since any unexposed plate can recover its original sensitivity after being bathed with phenosafranine, if washing with water is continued for a long time. It appears that desensitization is associated with the formation of an adsorption complex.

The loss in sensitivity on the ultra-violet side of 2200 Å is mainly due to the absorption of light by gelatin. Schumann (*Wiener Berichte* II A **102**, 994 (1893); *Ann. der Physik.* **5**, 349 (1901)) showed that plates made with as little gelatin as possible were sensitive to rays from 1250 to 2200 Å; these Schumann plates are used in vacuum spectroscopy, and rays from 50 to 2200 Å have been photographed in this way. Ordinary plates may be made sensitive to short ultra-violet rays by dissolving out a large proportion of the gelatin by sulphuric acid.

Duclaux and Jeantet (*Jour. de Physique* (VI) **2**, 156 (1921)) have described a very ingenious method for sensitizing plates to extreme ultra-violet rays. If a thin film of a highly fluorescent mineral oil (mobile oil, "Nujol" etc.) is spread over the surface of the ordinary plate, the very short wave rays emit fluorescent light, which, according to Stokes' law, is of longer wavelength than the exciting light, and thus the photographic plate is affected. An alcoholic or ethereal solution of the fluorescent oil is spread over the plate, which is then exposed to radiations of short wavelengths. After exposure, the plate is carefully washed with ether and alcohol to free it from oil, and then developed in the usual manner. By using a heavy mineral oil as sensitizer, Rossi and Bernardini (*Atti R. Accad. Lincei* (VI) **10**, 182 (1929)) have obtained photographic action on plates with low speed electrons of a velocity corresponding to 17.5 volts.

It has already been mentioned that Lüppo-Cramer (*Kolloid-Chemie u. Photographie*, p. 83 (1921)) has shown that certain colouring matters, and notably phenosafranine, diminish the sensitiveness of a photographic plate to such an extent that being exposed to light and then put into a solution of phenosafranine, it could be developed in diffused

light without fogging. Phenosafranine does not suppress all the action of light and render the plate simply insensitive, but it communicates to the plate some sort of inverse sensitiveness.

The mode of action of desensitizers is not known, but it appears to be of the same type as that of photosensitization, only the sensitized transformation is no longer the decomposition of the silver halide, but on the contrary, a reaction in which the liberated silver disappears and passes again into silver bromide. It should be stated that the disappearance of the latent image in presence of phenosafranine is favoured by potassium bromide.

According to Lüppo-Cramer, highly sensitive emulsions contain more "silver nuclei" or sensitivity centres, which might be thought to be connected with the gravimetrically determined excess of silver ions which always exist in the emulsion layer after decomposition with nitric acid. To test this, Schmidt (*Z. wiss. Phot.* **26**, 86 (1928)) compared the sensitivity changes of a control plate washed in conductivity water, and of a plate washed in dilute solution of sulphuric acid and potassium dichromate, respectively, and the plates were dried, exposed and developed under identical conditions. The sensitivity of the dichromate plate was reduced with chemical and primary physical development to an extent independent of the gravimetrically determined silver values, but bearing a direct relationship to the sensitivity. This appears to be a development phenomenon for the secondary physical development (i.e. development after fixing); the dichromate treatment destroys the sensitivity centres. No accurate method is yet available for the determination of the excess of silver in sensitized plates. Treatment with dichromate has the same effect on plates sensitized with acid dyes as on unsensitized plates of high sensitivity; but with plates sensitized with basic dyes, the dichromate causes great reduction in sensitivity for all three forms of development. This is due to the decomposition of the complex compounds of the silver halide with the basic dye, which are much less stable towards dichromate than the silver compounds of the acid dye. Similar results were obtained by Schmidt and Pretschner (*Z. wiss. Phot.* **26**, 375 (1929)) with various emulsions, and it was observed that the amount of silver present after fixing was not equal to the amount in the control plate.

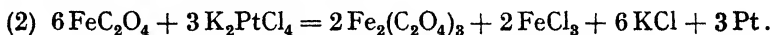
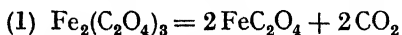
PHOTOSENSITIVE PAPER.

Papers containing silver salts. — These can be divided into two classes: (1) Papers which blacken directly and (2) papers which are to be developed.

1st class:— For obtaining a clear and brilliant image, the silver salt should not be simply deposited on the paper; it should be incorporated in an organic medium. Albumin was first utilized, but later on collodion has been used. At present, papers containing gelatin and silver chloride are used. There are numerous formulae for the preparation of the emulsion, which is formed by the generation of silver chloride, containing an excess of silver nitrate or citrate, and this facilitates the direct blackening. Sometimes the sensitizing action of certain substances such as resorcin has been utilized. The fixing is accomplished by thiosulphate, and the toning by a solution of gold or platinic chloride.

2nd class: *Papers to be developed*:— These papers permit considerable reduction of the duration of exposure. They are obtained by spreading on a piece of paper an emulsion of the same type as that used in the preparation of the plates, but ordinarily less sensitive. After a very short exposure, the paper is developed in the same way as a plate. Papers containing gallic acid as a developer in the emulsion have also been used. The reducing power of gallic acid should be decreased by the addition of sulphurous acid. A simple dipping in water is sufficient for developing the latent image. The fixing and the toning are done in the same way as with papers which directly blacken.

Papers containing platinum salts.—The salts of platinum are slightly photosensitive, but in presence of the ferric salts of organic acids, they are reduced by light, with the liberation of finely divided platinum. In practice, a paper impregnated with ferric oxalate and potassium chloroplatinite (K_2PtCl_4) is used. The ferric salt, under the action of light, is transformed into ferrous, which reduces the platinum salt. The following reactions take place:



The second reaction takes place with difficulty in dry paper. The image develops completely on immersion in a solution of potassium oxalate, which dissolves ferrous oxalate forming the complex salt, potassium ferrous oxalate. Potassium oxalate can also be incorporated in the sensitive paper. In this case, simple immersion in water suffices for the appearance of the image.

Papers containing iron salts. — These papers are not used in ordinary photography, but they are employed in rapidly obtaining images of marble models, industrial designs, etc.

In the *cyanotypes*, a paper impregnated with potassium ferri-cyanide, ferric oxalate, and tartrate is used. The ferrous salt, formed under the action of light, combines with the ferricyanide precipitating Turnbull's blue. The image is fixed by washing with water, which eliminates the ferric ferricyanide and other soluble salts.

In order to obtain blue marks on a white base, the property possessed by ferrous salt of rendering gums and gelatine impermeable is utilized. The paper is impregnated with gum arabic and ferric tartrate, and after exposure under the design to be reproduced, it is dipped in a solution of potassium ferrocyanide, which forms Prussian blue with the ferric salt, which is not acted upon by light; whilst those parts of the paper which have been acted upon by light are protected by the gum. A prolonged washing with dilute sulphuric acid eliminates the salts which have not been transformed.

Another process, which gives violet black marks on a white background, is based on the property of gallic acid of forming a dark compound (ink) with ferric salts which have not been acted upon by light. A paper containing gelatine impregnated with ferric tartrate or citrate and gallic acid is utilized. It is sufficient to expose the paper in the ordinary way, and wash it in water, for obtaining an image in which the parts protected from light appear dark coloured.

Papers containing carbon. — The carbon process, which was discovered by Poitevin, is based on the property of gelatin containing potassium dichromate of losing the power of dissolving in tepid water, after exposure to light. The bichromate is reduced by gelatin and forms Cr_2O_3 with the liberation of alkali, which forms chromate with the excess of bichromate. For preparing the paper containing carbon, bichromated gelatin is mixed with chinese ink (carbon), or coloured with another pigment, and spread out on a sheet of transparent paper. Light does not produce directly a visible image; but this appears on washing with tepid water, which dissolves the gelatine not acted upon by light. In order that the unchanged gelatin may dissolve and not be protected by the gelatin which has been rendered insoluble by the action of light, it is necessary to place the insensitive portion of the paper against the negative during the exposure.

COLOUR PHOTOGRAPHY.

From the earliest days of photography it was natural that people should dream of securing by its aid **photographs** in natural colours. Colour photography may be said to date back to the time of the

Farbenlehre of Goethe (1810). It is stated there that "if a spectrum produced by a prism is thrown on to moist silver chloride paper, if the printing be continued for 15 minutes, I observe the following: in the violet the chloride is reddish brown (sometimes more violet, sometimes more blue) and this coloration extends well beyond the limit of the violet; in the blue the chloride takes a clear blue tint which fades away becoming lighter in the green. In the yellow I usually found the chloride unaltered; sometimes, however, it had a slight yellow tint. In the red or beyond the red, it looks a rose or lilac tint. The image of the spectrum shows, beyond the red and the violet, a region more or less light and uncoloured. Beyond the brown band which was produced in the violet, the silver chloride was coloured a grey violet for a distance of several inches. In proportion as the distance from the violet increased, the tint became slighter. Beyond the red, on the contrary, the chloride took a feeble red tint for a considerable distance".

The discovery of colour photography has been attributed to the French physicist, the late Prof. Gabriel Lippmann, who stated in 1891 that he had succeeded in obtaining direct in the camera a true colour image of the solar spectrum, and that the results were permanent. However, there were other workers in this field, and as a matter of fact, modern methods are not an evolution of the process worked out by Lippmann.

We have already seen that Seebeck tried to obtain an image of the solar spectrum by its action on silver chloride, which had been rendered gray by a preliminary exposure to white light. Several authors, notably Niepce de Saint-Victor, Becquerel, Poitevin, Zenker, Krone, and others tried to utilize this phenomenon for colour photography. In fact, no satisfactory result has been obtained by this method, and the colour differences are not truly reproduced. For example, if celluloid paper is used, the blue and the red colours are well reproduced, but the reproduction of the other colours is defective. Moreover, the white becomes black, and vice versa, and no satisfactory fixing agent could be obtained. An explanation of this phenomenon has been proposed by Wiener. This is based on the fact that the rays, which are absorbed, are chemically active. The preliminary exposure of AgCl has the effect of producing a mixture of several photochlorides having different colours. If monochromatic light, say red, acts on these photochlorides, it will be reflected by the particles of the same colour and absorbed by the others. Thus the particles which are not red are changed, and after a certain time only

the red photochlorides are left. Although the explanation contains some truth, it does not express the reality. It is difficult to admit that the action of monochromatic light is only destructive. Moreover, the colour change seems to be a very complex phenomenon, and, according to the experiments of Weigert, adaptation to changes of colour takes place not only with reflected light but also under certain conditions with transmitted light. Hence, the changes of colour observed by Seebeck could not be utilized in colour photography, which depends on an entirely different phenomenon.

LIPPMANN PROCESS.

It is well known that a monochromatic ray of light, which falls normally on a polished surface, interferes with the reflected ray and forms stationary waves, i.e. waves which rise and fall in the same spot without progressing. If the reflecting surface carries a photosensitive layer, it forms a system of alternately dark and clear fringes. On using a silver mirror covered with a collodion emulsion containing very fine particles of silver bromide, Wiener (1890) stated that the luminous maxima act on the bromide. At the crests of the waves the light action was at its maximum. The silver liberated on exposure to light and development forms a series of thin layers of deposit, the distance between any two layers being equal to half the wavelength of the active light. The Lippmann process of colour photography is based on this formation of layers charged with particles of silver. Viewed by transmitted light the result resembled an ordinary negative, but by various arrangements for viewing at the proper angle, the reflected light from the laminæ in the emulsion reconstructed the colour rays which formed them. The process was ingenious and interesting as a verification of certain theories of light and colour, but as practical method it was far too cumbrous to come into general use.

It is well known that the three following visual colour sensations are of fundamental importance:

Blue-violet	4000 to 5000 Å
Green	5000 to 6000 Å
Orange red	6000 to 7000 Å.

A glance at the spectrum shows a marked variation in the luminosity of the colours as seen by the eye. The following table indicates in the first column, the relative luminosities of some of the colours, and

in the second column, the light value of each, assuming the total light to be represented by 100.

Red	8	9.1
Orange	76	14.7
Yellow and Yellow green	100	39.6
Green and blue green	64	30.3
Blue and indigo	12	3.8
Blue-violet	7	1.3
Violet	4	1.2

Moreover, the chemical activity of these rays, as observed by the change in the sensitive emulsion of an ordinary photographic plate, varies enormously. To obtain on an ordinary plate the same amount of density as would be given by white light, the relative exposures for lights of other colours would be as follows: Green 4, yellow 36, orange 120, red 1600.

This difference between the effect of coloured rays on the eye and on the ordinary plate was a great stumbling block in working out any method of colour photography. This difficulty was overcome by two means. It was soon discovered that certain dyes rendered the emulsion of an ordinary plate more sensitive to yellow and green, and plates so treated were known as ortho- or isochromatic. It was necessary to carry the sensitiveness still further, to include the red end of the spectrum as well, and hence the necessity of having panchromatic plates, which could be used in colour photography. Unfortunately a panchromatic plate is disproportionately sensitive to the blue, violet, and ultra-violet rays — the very rays that are least luminous, or even invisible to the eye. Hence, in actual practice a colour screen or filter is used, through which all light has to pass before reaching the plate. This filter is generally of a yellow colour, so that it cuts off or obstructs a certain proportion of the rays at the violet end of the spectrum, while allowing free passage to the visually brighter rays at the middle and towards the red. Thus in all colour photographic processes the use of a panchromatic plate and a colour filter is imperative, in order that the results shall correspond to the original visual effect. It is not sufficient to use any filter and any plate in conjunction; the two must be carefully adjusted. It is also necessary to have filters of different character for each kind of artificial light, such as electric arc, filament lamps, incandescent gas, etc.

According to the Young-Helmholtz theory of visual colour, any colour perception is the result of three primary sensations (red, green,

and blue) in various combinations and proportions. This is the basis of colour photography. It will be noticed that in all the screen-plate processes the same three colour elements are employed — red, green, and blue. In the screen itself, only these colours are found. All the resulting hues and tints in the final result are due to the extent to which these colours are allowed to take effect. The correspondence between this and our ordinary perception of colour is exact. An orange, seen in daylight, has its characteristic colour, because it absorbs or suppresses certain rays and reflects to the eye only those particular rays which, in combination, create the sensation of orange colour. In a colour photograph of an orange, we have taken steps which ensure that only those same rays reach the eye. A piece of ruby glass is red by transmitted light because it passes only those rays which collectively create that colour sensation in the brain through the medium of the eye. The same colour in a photograph is produced by suppressing all but those very rays.

MODERN PROCESSES.

We shall now consider the trichromatic method of colour photography adopted by Mr. F. E. Ives of Philadelphia, who used a triple lantern. The three lenses of the lantern were so arranged that they would project three discs side by side; but by a mechanical device it was possible to superpose either or both of the outer discs upon the middle one. Each lens was filled with a brightly coloured glass, the respective colours being roughly indicated as red, green, and blue. These brilliant discs were projected side by side and then superposed. The resulting single disc was almost white. If the light from each of three lenses could be completely obstructed, it would be possible to produce the following effects, according to the coloured lights projected:

R	G	B	White'
R	Red
R	..	B	Purple
R	G	Yellow
G	Green
G	B	Blue green
	B	Blue
	Nil	Black

Instead of the colours being completely obscured, they could be partially cut off or damped down, by interposing such varied gradations of density as are seen in the negative, and by this means all

other hues and tints could be produced. Mr. Ives made three separate negatives of the subject through three colour filters — say red, green, and blue — corresponding to the three colour sensations. As a rule, these negatives were taken successively, side by side, on one plate, but special cameras have been devised fitted up with mirrors in such a way that the image is simultaneously received on three different plates or films. The negative made through the red filter gave gradations corresponding to the degree to which the photographed objects reflected rays included in the red sensation. A transparency from this negative behind the lantern lens with the red glass would therefore give on the screen the correct values of the red elements of the subject. A similar result would follow with the transparencies from the green and blue sensation negatives. The result when the three images were superposed was a picture in true natural colours and light and shade.

A process dependent on the making of three negatives was developed by Mr. E. Sanger-Shepherd; in this case it was possible to produce a single colour transparency for projection by the ordinary lantern. This process gives excellent results. When the three negatives are finished, the first step is to make a black tone lantern slide from the red filter negative, and by means of a special solution the black image is changed to greenish blue. Two positives are then made by printing simultaneously from the green and the blue violet filter negatives. These positives are made on a special celluloid film, coated with gelatin containing silver bromide, and sensitized with a solution of potassium bichromate. Exposure is made through the celluloid, and the visible image resembles that of a platinum print before development, or of a print in bichromated gelatin for the oil-printing process. Immersion in warm water dissolves the unexposed portions of the gelatin, leaving a positive in white. Fixing in sodium thiosulphate removes the bromide of silver and leaves a colourless gelatin relief. The two positives are then washed, and are ready for staining. The positive from the green filter negative is dyed pink, and that from the blue violet negative, yellow. When the stained films are dry, they are superposed on the greenish blue lantern slide, and bound up with a mask and cover glass as in the case of an ordinary slide. An improvement is effected by using Canada balsam to cement the films in optical contact. The new point that emerges concerns the colours of the positive images. In the Ives triple projection, the colour of each positive corresponds roughly with the colour of the filter through which its negative was made; in the Sanger-Shepherd

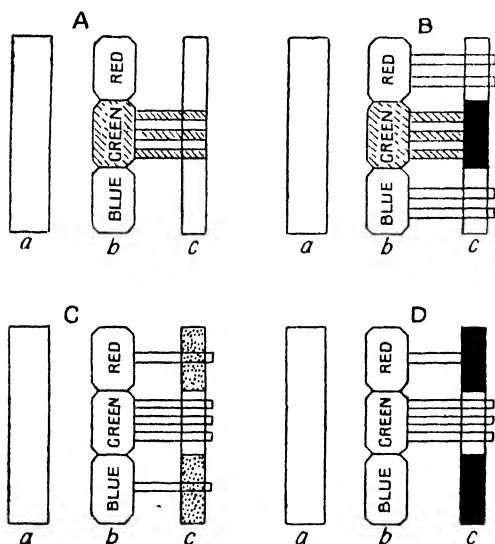
process the colour of each positive is complementary to the filter colour of its negative.

In the Ives process one kind of coloured light is added to another coloured light, so that the total rays constituting white light are added. If instead of three lenses only one was used, and the light projected into the three colour screens superposed, no light would emerge. The rays not stopped by one coloured glass would be stopped by another. Similarly, if red, green and blue pigments were applied one over the other, the result would approximate to black. In the former case, each of the three screens is contributing certain colour rays, and this is the additive method; in the latter, each of the three is obstructing certain rays and this is the subtractive method. Consider the case of a negative made through the red filter, the denser parts of this represent the action of the red rays that have reached the plate; therefore a transparency from the negative records the red effect by its clearer parts. Consequently, if light passing through the clearer parts also passes through a red glass the proper red effect will be projected on to the screen. But, if from the same negative an image in gelatin is made as in the Sanger-Shepherd process, this image is made through the clearer parts of the negative—the parts that have not recorded red rays—and it must therefore be stained to the complementary greenish blue. The same principle is utilized in the methods of making a three colour print by the adsorption and transference of dyes, which Sanger-Shepherd and others have adopted. From the three negatives, positives are made in transparent gelatin as just described. The positive from the green filter negative is placed in a pink dye, which it adsorbs in proportion to the thickness and distribution of the gelatine. It is then squeezed down on to a sheet of wet gelatinized paper, which, in a few minutes, adsorbs the whole of the pink dye. The image from the blue filter negative is stained yellow, adjusted in exact register on the pink image, and left till this dye has also been adsorbed. Finally, the red filter negative record is dyed blue, and its colour transferred to the pink and yellow image.

In the well-known autochrome plate process of MM. Lumière of Lyons, grains of starch some seven millions to the square inch and uniform in size, are dyed orange red, green, and blue violet, and intimately mixed in the ratio 3, 4, and 2. These dyed grains are sifted on to a glass plate with a sticky surface and rolled flat. Any minute interstices are filled with black pigment. The mosaic of starch grains is varnished and then coated with a panchromatic emulsion. The plate is exposed through the glass, which must be perfectly clean,

so that all the light that reaches the sensitive film passes first through the screen of starch grains. This necessitates the placing of the plate in the dark slide in a way reverse to that for ordinary exposures, and a black card is used to protect the film from the springs on the septum of the slide. It also necessitates the reversal of the ground glass of the focussing screen.

A special light filter, adjusted to the plate, must be used. This slightly displaces the focal plane. If it is placed behind the lens, the displacement is almost equal to that caused by reversing the plate, so that, in this position no allowance need be made with cameras



of fixed focus, or which focus by scale. With visual focussing on a screen, it is immaterial whether the filter is behind or in front of the lens. The exposed plate may be developed in many ways, preferably with a standard solution of "quinomet" in complete darkness. The result is, of course, a negative image, and the subject appears in complementary colours. The negative silver image is next completely dissolved away in an acid permanganate bath, and

the plate redeveloped in daylight. This second development requires a reagent that will give an image in pure black and grays, and for this the "quinomet" solution is suitable. The result is a positive image composed of the silver unused in the negative, and the true colours now appear. It may or may not be necessary to intensify this image. If it is necessary, the plate must afterwards be fixed in a sodium thiosulphate solution. In either case, it is quickly washed, dried and varnished.

We shall try to illustrate the principles involved in the Lumière Autochrome process by the diagrams above copied.

In each case "a" represents the glass, "b" three coloured starch grains, and "c" the panchromatic film. The light is travelling from the left through the lens and the filter. The object to be photographed

is supposed to be an evenly illuminated plane surface of the same colour as the green starch grain. "A" shows that the only light reaching the sensitive film is that passing through the green grain. "B" indicates the condition after development, when a patch of opacity behind the green grain is observed. When examined by transmitted light there is no sign of green but rays are passing through both red and blue. This gives, in combination, the colour given by white light minus its green rays. As the rays are weakened by the unaltered emulsion, two emerging rays instead of three are shown. In "C" the negative image has been reversed. The metallic silver behind the green grain is dissolved and the green rays pass through the clear gelatin; but the deposit behind the red and blue grains is not sufficiently thick, and allows some light to pass through as shown by a single ray. This not only alters the character of the green but weakens it, as the condition is approximating to that of all the rays passing and thus giving white light. Intensification gives the result shown in green. The red and blue rays are now completely cut off by the dense silver deposit, and the green rays alone pass, giving the exact colour of the object.

An interesting fact early observed about the autochrome plate was that of the reproduction of pure white. This could not be accounted for from the view of the unobstructed passage of light through all the starch grains. Lindsay Johnson discovered that in such parts, the photographic film showed a large number of silver particles which scattered the light, so that any suggestion of colour was entirely removed.

An objection that has been raised against the autochrome plate is that there can be no duplication of the result without exposing more than one plate; that one exposure means one colour transparency, and no more. This objection is not valid. From a successful experiment it is possible to make any number of replicas by copying on other autochrome plates, either by daylight, or by an apparatus employing magnesium ribbon as illuminant. It is also possible to fix a plate after first development, and hence maintain a negative from which positives can be directly made. Many of the finest specimens of colour photography exhibited by MM. Lumière are not originals but copies.

One of the simplest of screen plates was that introduced by Professor Joly of Dublin in 1894. He prepared a screen ruled with parallel lines about 150 to the inch, with orange, blue, green, and blue colours. A panchromatic plate was exposed with its film in contact with the

screen. From the negative a positive was made, and this was bound up with a similarly ruled screen having red, green, and blue-violet colours. As a ruled plate sets up diffraction, the colours given by such plates are often impaired by the production of a number of confused spectra.

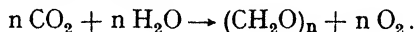
The Thames plate of C. L. Findlay has a pattern of adjacent circles in red and green, with blue interspaces. The popular Paget screen plate with coloured squares, about 40,000 to the square inch, is the next step. This could be used either by coating emulsion on the screen, as in the autochrome process, or by using a separate transparency and screen, as in the Joly process. The latter method is in greater use. The Paget process gives very beautiful results, but accurate registration is difficult.

Colour photography has been applied to cinema photography in various ways.

CHAPTER XXVIII.

Carbon Assimilation in Plants and Reduction of Carbon Dioxide.

Under the action of visible rays, green plants absorb carbonic acid gas and transform it with the aid of water into starch. We do not know as yet the exact mechanism of this change, which has been expressed by the following equation:



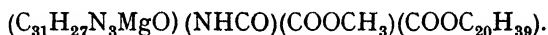
The reaction is endothermic. The quantity of energy absorbed is approximately 110,000 gram calories for each gram molecule of CO_2 reacting. In this photochemical process, light energy is converted into chemical energy, and the phenomenon leads to the accumulation of food materials in the plant kingdom, and of the energy utilized directly or indirectly by animals and men for their existence. There is, then, on the surface of the earth, no other phenomenon of greater importance than that of carbon assimilation by plants. In plant life, the exact function of chlorophyll in inducing the reactions in the plant cells, appears to be mysterious. In recent years, two developments seem to indicate the way to further investigations. One of these is the quartz mercury vapour lamp with which ultra-violet radiations for experimental purposes can be readily obtained, and the other is the use of fluorescent substances capable of absorbing light of one wavelength, and emitting it as radiation of another wavelength.

It should be stated that the photosynthesis of starch can be effected in certain plants under the influence of other pigments besides chlorophyll. Thus Wurmser has shown that the phycoerythrine of red algae is capable of carbon assimilation in diffused light. On the other hand, the formation of starch is not the only synthesis produced by light in plant life. The experiments of Laurent and collaborators (*Bull. Acad. roy. Belg. classe des sciences* (1896) and (1903)) appear to indicate that the formation of albuminous substances from nitric acid or ammonia requires the intervention of light. According to Dony-Hénault (*Mémoires de l'Acad. roy. Belg. t. III* (1911)), this transformation is catalyzed by manganese and iron salts.

Because of its practical importance, carbon assimilation has been the object of numerous researches. Priestley was the first to observe the liberation of oxygen from CO_2 in presence of green plants and light. The observations of Ingenhousz (1779—1800), Senebier (1782), and de Saussure (1804) have furnished data showing that the velocity of assimilation depends on the experimental conditions.

CHEMICAL COMPOSITION OF CHLOROPHYLL.

We owe to Willstätter and his colleagues (*Untersuchungen über Chlorophyll*, Berlin (1913)) almost all the information regarding the composition and the chemical properties of chlorophyll. In all green plants, the pigment is practically the same. Stokes stated in 1864 that the green colouring matter of plants consists of a mixture of two distinct but chemically related substances — chlorophyll (a) of blue green colour, and chlorophyll (b) of yellow green colour. These coloured substances can be separated by their different solubilities in petroleum ether or ethyl alcohol. The composition of chlorophyll (a) is represented by the formula $(\text{C}_{31}\text{H}_{29}\text{N}_3\text{Mg})(\text{NHCO})(\text{COOCH}_3)(\text{COOC}_{20}\text{H}_{39})$ and chlorophyll (b) is formed by the replacement of two hydrogen atoms by an oxygen atom:



There is no doubt that the presence of magnesium is necessary, but its rôle in the phenomenon of assimilation is unknown, and it is not clear how this metal is linked in the molecule.

ABSORPTION SPECTRA OF CHLOROPHYLL.

It has been well known for a long time that the absorption spectra of chlorophyll contain two bands in the visible, one in the red and the other in the violet portion of the spectrum. Wurmser (*Archives des Phys. biologique* 1, 33 (1921)) has carefully measured the absorption spectra of chlorophyll (concentration 0.0001 mol) in acetone solution. The red band has its maximum at 6700 Å, and the violet at 4300 Å. The constant of absorption corresponding to the second absorption maximum is about 3 times as great as the maximum in the red. The minimum of absorption is found in the green near 5500 Å. Beer's law is applicable to these solutions only as a first approximation. The chlorophyll existing in the colloidal state in leaves absorbs less than chlorophyll in the dissolved condition. Moreover, the spectra are not the same in the two cases. As in the case of chlorophyll in the

dissolved state, the minimum of absorption in the colloidal state is in the region 5500 Å; but the band situated in the red is a little displaced and the maximum is at 6500 Å. In the colloidal condition the band in the blue violet region is no longer simple, but presents two maxima, and results from the superposition of the simple band of chlorophyll upon a triple band of lipochrome.

DECOLORIZATION OF CHLOROPHYLL.

A solution of chlorophyll in alcohol, ether, acetone, etc. is decolorized rapidly under the action of light. This decolorization first investigated by Senebier (1782) is only produced in presence of oxygen and is a result of oxidation. In most plants the pigment is very stable, and the experiments of Willstätter and Stoll (*Untersuchungen über die Assimilation der Kohlensäure*, Berlin 1918) have shown that under strong light the chlorophyll content of leaves does not change. Wiesner, Stokes, Pfeffer, Wager, and others have supposed that the stability of the pigment in the leaves is only apparent, and that it is constantly regenerated at the same time as it is being destroyed. It appears, however, certain that the colloidal condition of the pigment leads to a certain amount of stability towards light. The colloidal chlorophyll obtained by the addition of water to an acetone solution of chlorophyll is more stable under the action of light than are true solutions.

According to Stoklasa (*Strahlentherapie* 6, 119 (1915)), young leaves of etiolated seedlings of pismu, zea mais, avena, and hordeum showed a dark green coloration after two hours' exposure to ultra-violet light and after six hours' exposure to sunlight. Bierry and des Bancelles (*Compt. rend.* 153, 124 (1911)) have shown that when alcoholic solutions of chlorophyll are exposed for a long time to ultra-violet radiations, the solutions become faintly yellow, and no longer show the absorption bands characteristic of chlorophyll. We have observed that in sunlight alcoholic solutions of chlorophyll are decolorized on exposure for 3 or 4 hours. According to Dangeard (*Compt. rend.* 156, 1844 (1913)), when a mixture of chlorophyll and pinaverdol is exposed to light, the chlorophyll is first decolorized, and the latter is destroyed through the energy absorbed by the chlorophyll, and not by that absorbed by itself. It appears that radiations, which are completely inactive towards a pure substance, are found to become active in the presence of a second pigment. A method of demonstrating the production of aldehyde by chlorophyll and by aniline dyes in the presence of sunlight has been described by Osterhout (*Amer. J. Botany* 5, 511 (1918)).

Gaffron (*Ber.* **60**, B, 755 (1927)) has shown that under the influence of light, a solution of chlorophyll in acetone absorbs oxygen with gradual oxidation of chlorophyll. In presence of a suitable acceptor the absorption is accelerated, and the chlorophyll suffers much less change. In presence of allyl thiocarbamide as acceptor, the relationship between the volume of oxygen absorbed and the amount of light used shows that in this case Einstein's photochemical equivalent law is obeyed for a large range of the spectrum. Confirmation is afforded of the observation of Warburg and Negelein (*Z. physik Chem.* **102**, 235 (1922)) that every quantum absorbed by the chlorophyll, independent of its energy, causes the same chemical action in the living plant.

Pfeilsticker (*Biochem. Z.* **199**, 12 (1928)) has advanced the view that chlorophyll (b), activated by four quanta, causes electrolysis of aqueous protein-carbon dioxide solution. Two carbonyl and two methine groups add on four hydrogen atoms, and bicarbonate and three hydroxyl ions are electrically discharged at the magnesium anode. Dipercarbonic acid is formed, which decomposes catalytically, giving formaldehyde and oxygen. The chlorophyll (a) regenerates chlorophyll (b) with the formation of hydrogen peroxide, from which catalase liberates oxygen.

The resistance to oxidation of a solution of chlorophyll is considerably increased by the addition of small quantities of gelatin, gums, and other substances, which render the precipitation of the colloidal substance by electrolytes more difficult. The substances which retard oxidation best are the very ones which stabilize the colloid most. According to the experiments of Wurmser, the great chemical stability of chlorophyll in presence of colloids appears to be due to the envelope formed by the colloid on the chlorophyll particles, and this process hinders the access of oxygen to the chlorophyll grains. The protoplasmic mass being a mixture of colloids, the chlorophyll grains in the leaves should be protected as in the artificially stabilized colloidal solutions.

Recently, Wurmser has carefully measured the velocity of decolorization of specially purified solutions of chlorophyll in radiations of different wavelengths, and has measured the amounts of incident and absorbed energies by a thermopile. Wurmser's results show that the velocity of the decolorization of chlorophyll is nearly proportional to the quantity of energy absorbed in red light. In violet light, the reaction is at first rapid but later on slows down; and after a few hours the reaction is practically stopped, although only a part of the chlorophyll is destroyed. If the velocity at the beginning of the reaction is taken into consideration, in case of violet light also the velocity is proportional to the

quantity of light absorbed. The following results have been obtained by Wurmser:

	Red	Green	Violet
Quantity of light absorbed (A)	50	2	29
Velocity of decolorization (v)	45	1.25	30
Ratio $v:A$	0.9	0.62	1.03
Absorption constant	0.46	0.09	1.31
	(6700 Å)	(5200 Å)	(4300 Å)
Susceptibility	0.41	0.056	1.34

It is seen that the photochemical yield for the same amount of light absorbed is nearly the same for red and violet rays, and markedly less for the green rays, which show a minimum absorption.

THE PROCESS OF CARBON ASSIMILATION.

In the first experiments on the variations of assimilation with the wavelength of light, a plant or a vegetable was exposed to sunlight with a coloured screen interposed between the plant or vegetable and the light. Thus Daubeney (1836), Cloez and Gratiolet (1851), Sachs (1864), Duhérain (1869) stated that the assimilation occurs mainly in the less refrangible part of the spectrum. More careful experiments by Timiriazeff (1869) showed that the maximum activity is situated in the red, and not in the yellow, as was formerly believed. Later on, Engelmann (1882) stated that there was a second maximum in the blue violet region, and this observation of Engelmann has been confirmed by Timiriazeff and by Kohl, but was not supported by Reinke or by Pfeffer. All these experiments had one defect. No attention was paid to the unequal distribution of the energy in different parts of the solar spectrum, or diffused light spectrum. Knieper and Minder, after taking into account the unequal distribution of energy in the solar spectrum, have stated that the activities of red and violet rays are practically equal; but these authors have not studied the assimilation process in green light, in which Timiriazeff obtained a velocity only one third of that in red light.

The researches of Wurmser have yielded more precise results. They have been carried out with the thallus of green algae (*ulva lactuca*), dipped in sea water and exposed to diffused light behind a coloured screen. The quantity of incident light was measured by an actinometric process. Knowing the constants of absorption of the thallus of green algae for different wavelengths, it was easy to calculate the quantity

of light absorbed by the chlorophyll. The following are the conclusions of Wurmser: The assimilation for the same amount of incident light, or, in other words, the susceptibility, is practically the same in red as in violet light; in green light (4600 Å to 5800 Å) the assimilation is only one third. The following results have been obtained by Wurmser when the quantity of light absorbed by chlorophyll is taken into consideration:

	Red	Green	Violet
Quantity of light absorbed (A)	100	6	34
Assimilation (v)	100	24	80
Yield ($v:A$)	1.0	4.0	2.35

FACTOR OF UTILIZATION AND QUANTUM YIELD.

The ratio of the quantity of the light energy absorbed to the amount which is transformed into chemical energy may be called the utilization factor, which has been determined with care by Warburg and Negelein (*Z. physik. Chem.* **102**, 248 (1922); *Naturw.* **13**, 985 (1925); **14**, 167 (1926)). They have carried out experiments with cells of algae (*Chorella vulgaris*) suspended in water saturated with CO_2 and O_2 . The quantity of light absorbed was measured by a bolometer. Contrary to the observations of Reinke (1883), and of Pantanelli (1903), on the assimilation process with the leaves of *Elodea*, where the velocity of photosynthesis increased proportionally to the intensity of light, Warburg and Negelein have obtained a decrease of yield when the light intensity is increased, and hence direct proportionality between light intensity and velocity of assimilation has not been observed. Measurements carried out under the same experimental conditions do not yield the same results with all cells of the same species. Cells which have been developed in intense light show more feeble yield than cells nurtured in weak light. In the yellow orange region of the spectrum (5700 to 6450 Å), and for cells chosen at random, the utilization factor is about 0.20; but with selected cells, the factor goes up to 0.70 or even to 0.85. According to Warburg, no other endothermal photochemical reaction shows such a high utilization factor. It should be remarked that the reduction of a molecule of CO_2 requires several quanta. For the orange rays (6100 Å), the product $Nh\nu = 45,000$ cal. Now we have seen that the transformation of a molecule of CO_2 requires 110,000 calories. If the absorbed light is totally transformed into chemical energy, 2.5 quanta ($110,000:45,000 = 2.5$) will be necessary for the reduction of a

molecule of CO_2 . In fact, the quantum yield never attains this value. When the factor of utilization is 0.70, the number of quanta necessary for transforming a molecule of CO_2 is 3.6, and this increases to 12 when the factor is 0.20. The results obtained by Warburg and Negelein on the variation of the utilization factor with the frequency are not in accord with the results of Wurmser (*Compt. rend.* **181**, 384 (1925)), who showed that the utilization factor increases from red to green (from 60% to 70%), whilst the data of Warburg and Negelein show a decrease from 60% to 44%, in agreement with Einstein's law. The difficulties underlying the determination of the photosynthetic efficiency are fully discussed by Briggs (*Proc. Roy. Soc. B* **105**, 1 (1930)). The author also discusses the results of Ursprung, Wurmser, and Warburg and Negelein.

The yield depends also on the temperature, for assimilation is a photochemical reaction which has a high temperature coefficient. This has been measured by Miss Matthaei (*Phil. Trans.* **197**, 47 (1905)), Blackman (*Ann. Botany* **19**, 281 (1905)), Kanitz (*Z. Elektrochem.* **11**, 689 (1905)), and recently by Warburg (*Biochem. Z.* **100**, 259 (1919)), whose results with an intense light source are as follows:

Temperature interval	5.4°—10°	10°—20°	20°—30°
Temperature coefficient for a 10° rise	4.3	2.1	1.6

The temperature coefficient varies considerably with the experimental conditions: all conditions remaining the same (when the carbon dioxide concentration is very high) Warburg found a high temperature coefficient of the order of 2 when the light intensity is high, and a low temperature coefficient of 1 with low intensity of light. This different behaviour towards temperature has also been observed by Willstätter and Stoll in the case of the green and yellow varieties of the same species. It was found that the rate of photosynthesis of normal green leaves of *ulmas* exposed to strong light, and in an atmosphere containing excess (45% of carbon dioxide), is more influenced by temperature than that of the yellow varieties of the same species.

The above results seem to suggest that photosynthesis consists of two stages, a photochemical and a thermal stage. When the light intensity becomes feeble, the temperature coefficient also decreases with increase of temperature, and tends to become unity between 25° and 30°, and the velocity of assimilation becomes independent of temperature.

THEORY OF CARBON ASSIMILATION.

For a long time this problem was looked upon exclusively as a question of pure chemistry, and the rôle of the living medium in which the assimilation was effected was neglected. The function of the medium has been brought into prominence by Blackman, Willstätter, and Stoll and Wurmser. On the other hand, the laws controlling the phenomenon are actually much better known than before.¹ There is no doubt that chlorophyll plays the part of a photosensitizer. The view that chlorophyll is constantly destroyed and regenerated by light, and constitutes in some manner or other an intermediate product in the assimilation process has to be given up, thanks to the researches of Willstätter and Wurmser on the oxidation of chlorophyll, already discussed.¹ Moreover, the fact that the absorption spectrum of chlorophyll coincides in important points with the spectrum of the photochemical sensitiveness, indicates clearly that the light absorbed by chlorophyll indirectly causes the reduction of CO_2 .¹ It seems certain, therefore, that chlorophyll behaves as an optical sensitizer, but its mode of action is still unknown.¹

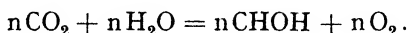
Moore and Webster (*Proc. Roy. Soc.* **90**, 168 (1918)) have shown that solutions or emulsions of mono-, di-, and poly-saccharides, glycerol, chlorophyll, egg albumin, milk, and vegetable juices yield formaldehyde on exposure to ultra-violet rays for 3 to 4 hours; sunlight causes the same change, but requires a longer time. The change takes place far more slowly in glass than in quartz containers, and the more transparent the solution, the more marked is the reaction. The germicidal power of sunlight, and certain other phenomena, are supposed to be related to this generation of formaldehyde.

Kogel (*Biochem. Z.* **95**, 313 (1919)) states that tetrahydroxyethylene is considered to be an intermediate product in the formation of formaldehyde from carbon dioxide. Keto-enol changes are supposed to play an important part in the photosynthesis of formaldehyde and sugar.

Reinhard (*Compt. rend. Soc. Biol.* **89**, 1274 (1923)) has noted that leaves of beans, peas, and white acacia produce starch when immersed in a 10% sugar solution and exposed to light, and Sabalitscha and Riesenbergl (*Biochem. Z.* **144**, 545 (1924)) have reported that certain plants assimilate formaldehyde in the dark with the formation of sugar and starch.

Willstätter and Stoll proved that within narrow limits the volume of oxygen given out is equal to the volume of carbon dioxide absorbed

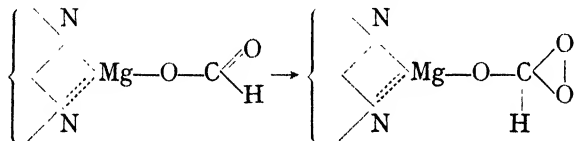
by the leaf. However, according to Kostytschew (*Ber. bot. Ges.* **39**, 319 (1921)), the ratio CO_2/O_2 during illumination varies with time. During photosynthesis the leaves absorb initially carbon dioxide in much larger volume than they give off oxygen; about one third the absorbed carbon dioxide is fixed without oxygen emission. After a short time these conditions are reversed, and finally the CO_2/O_2 ratio attains a constant value of 1. These results suggest that oxygen evolution probably takes place in two stages. The results of Willstätter and Stoll are in conformity with the following equation:



The importance of the rôle of the pigments, carotin, xanthophyll, chlorophyll "a", and chlorophyll "b" has been minimized, owing to the demonstration that the velocity of assimilation changes but slightly when the concentration of chlorophyll is varied considerably. Moreover, the experiments of Willstätter and Stoll, and of Kremann and Schniderschitsch (*Monatsh.* **37**, 659 (1916)) show that although chlorophyll adsorbs carbon dioxide to a certain amount, the extent of this adsorption is insignificant in comparison with that which occurs with green leaves, namely 150—170 molecules of carbon dioxide per molecule of chlorophyll. The ratio $\text{CO}_2/\text{O}_2 = \text{unity}$, as observed by Willstätter and Stoll, would appear to indicate that formaldehyde in some form or other should be the primary product, which may be very reactive or unstable.

It is generally agreed that formaldehyde is an intermediate product in this photosynthesis, and that this is transformed into hexose by polymerization. Recently, Jörgensen and Stiles (*Scientia* **25**, 196 (1919)) have stated that the formation of formaldehyde is not beyond doubt. The photosynthesis of formaldehyde by the action of ultra-violet light on a mixture of $\text{CO} + \text{H}_2$ (Berthelot and Gaudechon), $\text{CO}_2 + \text{H}_2$ (Stoklasa and Zdobnicky), or on an aqueous solution CO_2 (Usher and Priestley) does not prove that formaldehyde is formed in carbon assimilation, which takes place under entirely different conditions. Similarly, the photosynthesis of formaldehyde has been observed by Bach, Moore and Webster, Baly and collaborators, and Dhar and Sanyal, by the action of visible light on an aqueous solution of CO_2 in presence of photosensitizers such as ferric or uranium salts, malachite green, methyl orange, colloidal ferric hydroxide, uranium hydroxide, etc. This fact has, however, been contested by Baur (*Helv. Chim. Acta* **5**, 828; **6**, 959 (1923)), who has repeated the experiments on the formation of formaldehyde in presence of malachite green. Recently, Baly and co-

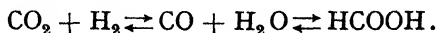
workers (*Proc. Roy. Soc. A* **116**, 197, 212 (1927)) have denied the formation of formaldehyde from CO_2 and water in ultra-violet light. The direct assimilation of formaldehyde by plants is not definitely proved; from the fact that a substance can serve as a food for plants it need not be concluded that it should be produced in the assimilation process. However, it is an index of some value. On the other hand, the presence of formaldehyde in leaves, which shows normal assimilation, seems to have been actually demonstrated, and the recent experiments of Klein and Werner (*Biochem. Z.* **169**, 361 (1926)) seem to indicate that the existence of formaldehyde in leaves is not due to the photochemical decomposition of certain substances existing in plants, as has been suggested by Jörgensen and Stiles, but that it is really an intermediate product of assimilation. In order to explain its formation in plants, Willstätter and Stoll have assumed that a molecule of CO_2 forms with chlorophyll a complex compound, which transforms under the action of light into an isomeric peroxide.



This isomeric substance decomposes spontaneously, or under the action of a catalyst contained in the leaves, giving out oxygen. Willstätter and Stoll, however, were unsuccessful in imitating these reactions in the laboratory. For some years the view has been gaining ground that the oxygen is not liberated in immediate contact with the chlorophyll. Several authors have arrived by different methods at the conclusion that CO_2 does not play a part in the primary phenomenon, and is only reduced in the secondary reactions which take place outside the leucites (compare, Thatcher, *J. Ind. Eng. Chem.* **14**, 1146 (1922)).

REDUCTION OF CARBON DIOXIDE.

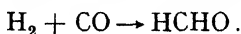
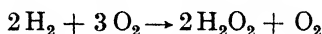
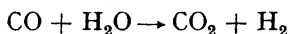
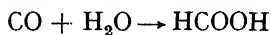
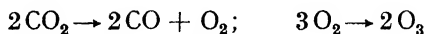
Let us consider some chemical reactions of carbon dioxide. Ballo (*Ber.* **17**, 7 (1884)) was the first to convert carbonic acid to formic acid by sodium amalgam. Bredig and Carter (*Ber.* **47**, 541 (1914)) investigated the following equilibrium at different pressures and in the presence of different catalysts:



No indication of the formation of formaldehyde was obtained by them. Fenton (*J. Chem. Soc.* **91**, 687 (1907)) reduced carbonic acid directly

to formaldehyde by metallic magnesium, and the presence of weak alkalis favours this reduction. Formic acid may also be reduced to formaldehyde by magnesium.

The influence of the silent electric discharge on a mixture of carbon dioxide and water is likely to be allied to photochemical reactions, and has been extensively studied. Losanitsch and Jovitschitsch (*Ber.* **30**, 135 (1897)) and Löb (*Z. Elektrochem.* **11**, 745 (1906)) state that the following reactions are likely to occur in the silent electric discharge:



Glycollic aldehyde was obtained by Löb by the reaction of CO and H₂. It will be interesting to note that α -particles, β -rays, and the corona discharge in carbon dioxide and water vapour do not cause the formation of formaldehyde or formic acid (compare Lunt, *Proc. Roy. Soc. A* **108**, 172 (1925)).

Cochin and collaborators (*Z. physik. Chem.* **91**, 347 (1916)) have shown that dry carbon dioxide is decomposed by extreme ultra-violet radiations. The following absorption results were obtained by Kreuler:

Wavelength	Per cent absorption by CO ₂
2000 Å	1.8
1930 Å	4.0
1860 Å	13.6

Herschefinkel (*Compt. rend.* **149**, 395 (1909)) and Berthelot and Gaudechon (*ibid.* **150**, 1690 (1910)) effected the following decomposition: dry CO₂ \rightleftharpoons CO + O₂; and in presence of hydrogen the following photochemical reaction took place:



Chakravarti and Dhar (*Z. anorg. Chem.* **142**, 299 (1925)) have shown that several colouring matters behave as mild reducing agents in light under suitable conditions. Similarly, chlorophyll can function as a reducing agent. Gopala Rao, and Dhar have now shown that the amount of CO obtained from CO₂ in presence of light from a 500 Watt tungsten filament lamp is considerably greater in the presence of chlorophyll

than in the absence of it. The carbon monoxide was tested for by the iodine pentoxide method.

Usher and Priestley (*Proc. Roy. Soc. B* **84**, 101 (1911)) obtained a positive test for formaldehyde by using CO_2 and water in a quartz vessel. Stoklasa and Zdobnický (*Biochem. Z.* **57**, 110 (1911); **44**, 330 (1913)) did not obtain a positive test for formaldehyde or sugar when CO_2 and H_2O were irradiated, but formaldehyde was observed when CO_2 and H_2 and KOH were illuminated with short ultra-violet radiations.

Spoehr (*J. Amer. Chem. Soc.* **45**, 1184 (1923)), by changing the type of mercury vapour lamp, temperature, pressure of carbon dioxide, time, and distance of exposure, Coehn and Sieper (*Z. physik. Chem.* **91**, 347 (1916)), Chadwick, Chapman, and Ramsbottom (*J. Chem. Soc.* **91**, 94 (1907)) Baur and Rebmann (*Helv. Chim. Acta* **5**, 828 (1922)), and Porter and Ramsperger (*J. Amer. Chem. Soc.* **47**, 79 (1925)) obtained negative results regarding formaldehyde formation. Porter and Ramsperger have concluded that if formaldehyde is formed from CO_2 and H_2O alone on illumination, the reaction is reversible, and the formaldehyde is decomposed as fast as it is formed.

On the other hand, Dhar and Sanyal (*J. Phys. Chem.* **29**, 926 (1925)) have obtained formaldehyde by passing carbon dioxide into beakers containing conductivity water exposed to tropical sunlight. The formation of formaldehyde is facilitated by methyl orange, methylene blue, ferric chloride, uranyl salt, chromium salt, ferric hydroxide sol, chlorophyll, etc. Similarly, Mezzadrolì and Gardano (*Atti R. Accad. Lincei*. (VI) **6**, 160 (1927)) have also obtained formaldehyde and small amounts of sugar by exposing solutions of bicarbonates of different metals to ultra-violet light. Ammonium bicarbonate gives a greater proportion of formaldehyde than the alkali hydrogen carbonates, but the greatest yield of formaldehyde is obtained from calcium hydrogen carbonate. The amount of formaldehyde formed rises to a maximum and then gradually diminishes, owing to oxidation and polymerization. Moreover, Mezzadrolì and Vareton (*Zymologica* **3**, 165, (1928)) have shown that exposure of these bicarbonate solutions to ultra-violet rays results in increase of the reducing power of the solutions to a maximum, followed by rapid decrease. Under similar conditions, solutions of carbon dioxide prepared by continuous passage of the gas through water, show progressive increase in reducing properties. The presence of colloidal or reducing catalysts increases the maximum reducing powers. Mezzadrolì and Vareton (*Atti R. Accad. Lincei* (VI), **8**, 511 (1928)) have also reported that the yield of form-

aldehyde and sugars is increased by the addition of metallic magnesium to the calcium bicarbonate solutions. Recently, Mezzadrolì and Babes (*Gazzetta* **59**, 305 (1929)) have stated that the reducing power of a 5% solution of potassium hydrogen carbonate exposed to the action of ultra-violet rays increases to a constant value in presence of active carbon "norit", instead of rising to a maximum and then decreasing, as previously found in the absence of carbon. When zinc is present with the carbon, the reducing power is still further increased. It appears that the adsorption of carbon dioxide and hydrogen on the surface of carbon particles brings about a more intimate contact, and facilitates the reaction between the two gases.

Recently, the experiments of Sanyal and Dhar (*J. Phys. Chem.* **29**, 926 (1925)) were contradicted by Burk (*J. Phys. Chem.* **31**, 1338 (1927)). Gopala Rao, and Dhar have now repeated some of the experiments, and the following results have been obtained:

1. CO ₂ and conductivity water sealed and exposed for 60 hours to sunlight in glass tubes.	Very small quantities of HCHO.
2. CO ₂ and conductivity water + Fe(OH) ₃ sol (exposed for 60 hours)	Small quantities of HCHO and carbohy- drate.
3. 2% solution of NaHCO ₃ + a little cobalt sulphate 40 hours' exposure.	Small quantities of HCHO.
4. 2% solution of NaHCO ₃ + a little nickel sulphate 45 hours' exposure.	Small quantities of HCHO and carbohy- drate

The solutions were distilled, and the distillates tested for formaldehyde with Schryver's reagent, and with modified Schiff's reagent described by Denigès (*Compt. rend.* **150**, 529 (1910)). Blank experiments were done in every case, great precautions being taken to prevent the introduction of organic matter.

In 1887 Pringsheim (*Sitzungsb. d. preuss. Akad. d. Wiss.* **38**, 1887)) observed that the cells of *Chara* exposed to light in a current of hydrogen and CO₂ do not absorb CO₂. The necessity for the presence of oxygen has been confirmed by Ewart, and Willstätter and Stoll. Pringsheim has drawn the conclusion that in the photosynthesis oxygen is not liberated in the vegetable tissue, but that there is the primary formation of an intermediate unstable compound, which diffuses in the leaves and is only decomposed on the surface, giving up oxygen. Wurmser, however, assumes that the existence of such a substance is improbable,

because the vegetable tissues possess a powerful reducing action. It is then difficult to admit that a substance, which is stable enough to escape the reduction, can liberate its oxygen at the surface of the leaves. However, on other grounds, Wurmser is in agreement with Pringsheim in the view that the origin of oxygen is outside the chlorophyll grain. These researches of Wurmser have shown that the resistance to the photo-oxidation of chlorophyll in the leaves should be ascribed to the colloidal material which hinders the access of oxygen to the chlorophyll grains. The formation of oxygen is thus excluded in the assimilation in contact with chlorophyll grains because if it were formed the pigment would be rapidly oxidized.

Blackman has indicated other reasons for searching in the protoplasm outside the chlorophyll for the seat of the reductions which regulate the progress of the starch synthesis:

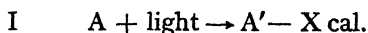
(1) The temperature coefficient of the chlorophyll assimilation is not that of an ordinary photochemical reaction, but resembles that of a thermal reaction.

(2) According to the observations of Willstätter and Stoll, the photosynthetic activity of leaves in different stages of development is very different. The quantities of CO_2 assimilated in a given time by a gram of chlorophyll are very variable, and this led Willstätter and Stoll to think that the photosynthesis depends not only on this pigment, but also on other agents of a catalytic nature.

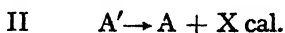
(3) The capacity to reduce CO_2 possessed by the green pigments of a plant is not unique.

Moreover, Osterhout and Haas have observed that there is a period of induction in the assimilation process. The velocity, which is slow in the beginning of illumination, increases up to a limiting value, and then remains constant. They have concluded that the action of light is followed by a series of secondary reactions.

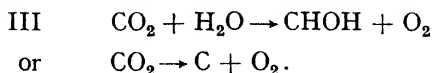
Wurmser has suggested the following scheme: A primary reaction by light in contact with chlorophyll grains. This reaction takes place with an unknown substance A , and it is endothermal so that it can be represented by the following equation:



The product A' diffuses in the stoma and undergoes a transformation in which A is probably regenerated:



The free energy liberated in this transformation makes the reduction of CO_2 possible according to either of the two reactions:



Basing on thermochemical considerations, Wurmser was led to think that the primary phenomenon (I) may be the dissociation of water.

As a first approximation it can be supposed that the velocity of the reaction (I) increases proportionally to the quantity of light absorbed. The assimilation depends also on two other coupled reactions (II) and (III). Now, an increment of the concentration of A' has the effect of decreasing those of the substances (CO_2 or protoplasmic substances), which react with A . The velocity of assimilation depends not only on the quantity of light absorbed, but also on the velocity with which the bodies diffuse towards the leucites, or the substance A' is generated. This is how Wurmser explains that the green rays, which are feebly absorbed, give the maximum yield.

Warburg and Negelein (*Z. physik. Chem.* **106**, 191 (1923)) have also attributed the decrease of the yield when the intensity of light increases to a phenomenon of impoverishment.

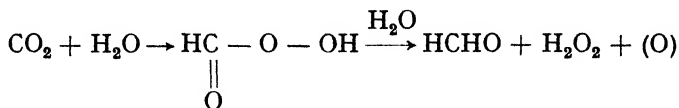
Considerations of a different order, based on the phenomena of oxidation in the living tissues, have led Thunberg (*Z. phys. Chem.* **106**, 305 (1923)) to believe also that the reduction of CO_2 is indirect. The primary reaction would be the decomposition of water according to the following equation: $2 \text{H}_2\text{O} + \text{light} \rightarrow \text{H}_2 + \text{H}_2\text{O}_2$. The hydrogen and hydrogen peroxide react with CO_2 forming formaldehyde: $\text{CO}_2 + \text{H}_2\text{O}_2 + \text{H}_2 \rightarrow \text{H}.\text{CHO} + \text{O}_2 + \text{H}_2\text{O}$.

This view has been accepted by Weigert (*ibid.* **106**, 313 (1923)), who has attempted to make the mechanism of the phenomenon of sensitization by chlorophyll more precise, and to explain the part played by oxygen in the primary process, the presence of oxygen being necessary for the occurrence of the assimilation phenomenon. The interpretation of Weigert is beset with difficulties regarding the energy relations. According to him, the necessary energy for the production of photosynthesis is furnished not only by light but also partly by the heat of the plant.

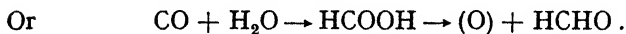
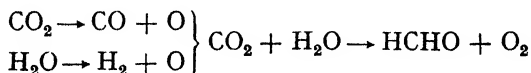
Wo. Ostwald (*Kolloid. Z.* **33**, 356 (1923)) has suggested that the photosynthesis occurs as a heterogeneous reaction, and that globulin is capable of forming globulin carbonate, or a globulin-carbon dioxide adsorption complex. Lipoid peroxides are assumed to play an important

part, and the seat of the reaction is the globulin-lipoid peroxide interface. Formaldehyde and oxygen are formed under these conditions.

Another view is expressed as follows:



Another possibility is suggested in the following reactions:



Recently, Ghosh (*Jahrb. wiss. Bot.* **69**, 572 (1928)) has derived a formula for the velocity of assimilation of carbon dioxide by the plant in light, on the basis of the theory of Willstätter and Stoll. The formula is applicable to the results obtained by Harder (*Jahrb. wiss. Bot.* **60**, 568 (1921)) on carbon dioxide assimilation.

Sayre (*Plant physiol.* **3**, 71 (1928)) has shown that wavelengths longer than 6800 Å are not effective in the formation of chlorophyll in maize, wheat, oat, barley, bean, sunflower, or radish seedlings. The effectiveness of radiant energy appears to increase with the wavelength to about 6800 Å, and then to fall abruptly to zero.

From the above summary of the actual condition of the problem of carbon assimilation, it will be clear that we are far from a complete and satisfactory explanation of the phenomenon. We are of the opinion that chlorophyll, over and above its photosensitizing effect, exerts a feeble reducing action on carbonic acid (*loc. cit.*). That chlorophyll takes some part in the reduction of carbon dioxide is indicated by the experiments of Warburg on the influence of carbon dioxide concentration on the rate of photosynthesis. With increasing carbon dioxide concentration above a certain amount, Warburg found that the increase in the rate of photosynthesis rapidly falls off until, at a certain concentration of CO_2 , further increase in the latter produces no effect. Warburg explains that the rate of photosynthesis depends not only on the concentration of CO_2 , but on that of some other substance (chlorophyll) as well, with which CO_2 reacts. The experiments of Willstätter and Stoll on chlorophyll content also suggest the same.

PHOTOSYNTHESIS OF NITROGEN COMPOUNDS.

According to Moore (*J. Chem. Soc.* **119**, 1555 (1921)), sunlight causes a slight union of nitrogen and oxygen in the air, resulting in the formation of oxides of nitrogen. Dhar and Sanyal (*J. phys. Chem.* **29**, 926 (1925)) have observed the formation of traces of nitrites when air freed from impurities is bubbled through conductivity water in presence of ultra-violet light.

Moreover, it has been shown by the above authors that although gaseous ammonia and oxygen form mainly nitrogen and water, aqueous ammonia and oxygen cause the production of nitrite when exposed to sunlight or ultra-violet light. Ammonium salts are also oxidized to nitrites, the reaction being slower in the case of the sulphate and chloride than with the carbonate. Nitrous oxide alone, or mixed with oxygen, produces nitric acid.

Recently Gopala Rao, and Dhar have observed that this oxidation of ammonia and ammonium salts in the presence of sunlight is photosensitized by various oxides, e.g. titania, zinc, and cadmium oxides, alumina, and silica. Titania is the most and silica the least active in this respect. The oxidation of ammonium compounds is very rapid in the presence of these oxides and sunlight; and it is apparently unaffected by the accumulation of the reaction product, namely, nitrite. The p_H of the solution has a profound influence on the reaction velocity; alkalinity increases and acidity diminishes the rate.

These experiments on the photochemical oxidation of ammonia seem to throw new light on the mechanism of nitrification in the soil. Hitherto it has been believed that this oxidation is mainly due to bacteria. It has been found by Omeliansky (*Centr. Bacteriol.* (2) **5**, 473 (1900)) that for the bacterial action a high concentration of ammonia or nitrite is harmful; about 0.3% of nitrite inhibits the process. Nevertheless, it has been found that in "nitre spots", the concentration of nitrites and nitrates rises to 5% of the bulk of the soil. The criticism to be made of the biological explanation, as being entirely sufficient for the accumulation of nitrites and nitrates, is that the high concentrations of nitrite formed should preclude the action of the nitrifying bacteria in the later stages. We now suggest that this nitrification in the soil is, at least in part, photochemical, taking place at the surface of various soil photocatalysts in sunlight. All soils contain alumina and silica, and according to Geilman (*J. Landw.* **68**, 107 (1920)), most fertile soils contain titania in quantities between 0.3—0.6%. The present theory satisfactorily explains the varying activities of different

soils noticed by McBeth and Smith (*Centr. Bacteriol.* (2) **40**, 24 (1914)). This is also in accordance with the observation that nitrification in soils is most active near the surface of the soil.

According to Baudisch (*Ber.* **49**, 1176 (1916); **51**, 793 (1918)) methyl alcohol reacts with potassium nitrite with the production of the potassium salt of formhydroxamic acid, in presence of ultra-violet light or sunlight.

Baly, Heilbron, and Hudson (*J. Chem. Soc.* **121**, 1078 (1922)) have stated that under the influence of ultra-violet or visible rays in presence of a photocatalyst, formaldehyde and nitrites react readily with the formation of formhydroxamic acid, which is the first step in the synthesis of nitrogenous compounds in plants. The photosynthesis of nitrogenous compounds from formhydroxamic acid is rapid, and amino-acids, pyrrol, and pyridine derivatives, condensing further to xanthine bases, and substances of an alkaloidal nature are formed.

After exposing ammonia solution saturated with carbon dioxide to the radiations from a quartz mercury lamp, Baly, Heilbron, and Stern (*J. Chem. Soc.* **123**, 165 (1923)) seem to have obtained methylamine, pyridine, etc.. If ammoniacal solutions of cupric carbonate saturated with carbon dioxide are used, methylamine and pyridine or piperidine are formed. When 2 M solutions of formaldehyde and ammonia are exposed to ultra-violet light for 6 to 10 days, a brown solid giving the reactions of the alkaloid conine is obtained, along with other products mentioned before. It appears that the complex products of photosynthesis are slowly decomposed by ultra-violet rays of short wavelength.

Snow and Stone (*J. Chem. Soc.* **123**, 1509 (1923)) have, however, stated that the evidence of Baly, Heilbron, and Stern for the formation of conine or pyridine is inconclusive, and that the products of the normal interaction of ammonium chloride and formaldehyde, tetramethylmethylenediamine and methyl methylene imine, have the same reactions.

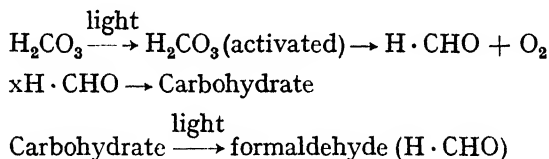
Hepworth (*Chemical Synthesis*, p. 12, Glasgow, Blackie and Son, 1924)) points out that the synthesis of proteins can also take place in the dark provided carbohydrate is available, and that nitrogen assimilation is not a photochemical process, light being of indirect importance in providing a means for the formation of carbohydrates.

Dhar and Sanyal (*loc. cit.*) have shown that methylamine, which is formed in about 12 hours in tropical sunlight when ammonia and formaldehyde solutions are exposed, passes into a number of complex nitrogenous substances on longer exposure.

Houben and Fischer (*Chem. Zentr.* 1, 2486 (1928)) have shown that formaldehyde in ultra-violet light forms reducing agents; methyl alcohol and potassium nitrite produce formhydroxamic acid. Instead of alkaloids, alkylamines were obtained.

BALY'S WORK ON THE INFLUENCE OF ULTRA-VIOLET LIGHT ON FORMALDEHYDE, CARBON DIOXIDE, AND MOISTURE.

Baly and collaborators (*Proc. Roy. Soc. A* 116, 197, 212, 219 (1927)) have shown that when a 40% formalin solution containing an excess of calcium carbonate is placed in a tank kept at 30°, and exposed to ultra-violet light from four quartz mercury vapour lamps for a month, and the mixture is stirred, 80% calcium formate, 5–6% calcium glycollate, and 15% of a complex mixture containing glycol, glycerol, pentaerythritol, and some reducing sugars are obtained. According to these authors, the action of ultra-violet light is represented by the following scheme:



It is assumed that the following stationary state is established by the action of ultra-violet light on carbonic acid: $6 \text{H}_2\text{CO}_3 \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2$. Where the concentration of carbohydrate is very small, and in presence of reducing agents, the reaction would proceed from left to right with the formation of carbohydrate, which would be photochemically decomposed to formaldehyde. Moreover, Baly and co-workers observed that when various sparingly soluble substances capable of adsorbing carbon dioxide were used, and carbondioxide was passed and the whole exposed to ultra-violet light, complex organic compounds containing carbohydrates, which char readily and develop reducing power after hydrolysis with hydrochloric acid, are formed. Among the powders which behaved in this way were metallic aluminium, barium sulphate, freshly precipitated aluminium hydroxide, and basic carbonates of magnesium, zinc, etc. They also used coloured substances, like nickel or cobalt carbonate, in aqueous carbonic acid and visible light. The organic material formed reduced Benedict's solution, gave the Molisch and Rubner reactions, and formed a solid

osazone. Under comparable conditions the use of visible light and coloured surfaces gave a greater yield of organic matter than the use of ultra-violet light and white surfaces, and also the carbohydrate content was higher. It appears that the exclusion of ultra-violet light prevents the photo-decomposition of the carbohydrates formed. If a solution of ammonium carbonate, containing a suspension of nickel or cobalt carbonate, is exposed to visible light, complex nitrogeneous organic compounds are formed.

Baly and collaborators point out that the thermochemical equation $6 \text{H}_2\text{CO}_3 \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2 - 673,800$ calories, demands minimum frequency of 1.1754×10^{15} , corresponding to the wavelength 2552 Å, for activation of carbonic acid by means of radiation alone. Since photosynthesis occurs in the plant with visible light, some other mode of activation must be discovered. These authors state: "The total quantity of energy necessary for photosynthesis to take place is supplied in two separate amounts, one quantity being given when the adsorption on the surface takes place, and the second quantity being given out by light".

It should be pointed out that a similar behaviour is observable with several other photochemical reactions, which are sensitized by different substances.

Recently, Baly and Hood (*Proc. Roy. Soc. A* **122**, 393 (1929)) have shown that if the yield of carbohydrates (weight of photosynthesized organic matter soluble in absolute methyl alcohol), obtained from the presence of specially purified suspension of nickel carbonate (50 grms.) in 1000 c.c. of water, is plotted against the temperature, the relation is found to be a linear one between 5° and 31° (maximum yield being 0.0783 grm.), after which there is a rapid decrease in yield. The values of the temperature coefficient for a 10° rise are in good agreement with those found by Warburg (*Biochem. Z.* **100**, 258 (1919)) with the unicellular alga *Chlorella* under constant illumination. Baly and Hood have pointed out the close analogy between the photosynthetic processes *in vitro* and *in vivo*, with special reference to the researches of Miss Matthaei (*Phil. Trans. B* **197**, 47 (1905), on the assimilation of carbon dioxide at various temperatures, and to the fact that the process, both in the living leaf and in the laboratory, has an upper and a lower temperature limit.

CHAPTER XXIX.

Some Biochemical Aspects of Light Action.

OXIDATION OF CARBOHYDRATES, FATS AND NITROGENOUS SUBSTANCES BY AIR IN SUNLIGHT: LIGHT THERAPY.

It has been shown by Dhar and Sanyal (*J. Phys. Chem.* **29**, 926 (1925)) that methyl alcohol, ethyl alcohol, and glycerol are oxidized by passing air at the ordinary temperature in presence of sunlight.

Palit and Dhar (*J. Phys. Chem.* **32**, 1263 (1928); **34**, 993 (1930)) have made a systematic investigation of the oxidation of various substances by air in sunlight. They have shown that different carbohydrates glycogen, urea, glycine, hippuric acid, α -alanine, sodium urate, potassium palmitate, stearate, oleate, sodium formate, tartrate, oxalate, lecithin, cholesterol, butter, milk, egg white, egg yellow etc., can be oxidized by passing air at the ordinary temperature in presence of sunlight. Tartaric, citric, lactic, and oxalic acids have also been oxidized. Glass bottles containing solutions of various substances were exposed to sunlight, and a definite volume of air was passed through them, and the amounts of unoxidized substances were estimated after passing 36.5 litres of air in $5\frac{1}{2}$ hours. Some of the experimental results are recorded below:

Substance used in the experiment	Weight of substance taken gram.	Amount oxidized gram.	Percentage amount oxidized
Arabinose	0.1000	0.0075	7.5
Galactose	0.0861	0.0067	7.8
Cane sugar	0.0964	0.0098	10.2
Glucose	0.0962	0.0144	14.9
Laevulose	0.0918	0.0159	17.3
Lactose	0.0977	0.0197	19.7
Maltose	0.1097	0.0285	25.9
Starch	0.1027	0.0399	38.8
Glycogen	0.0987	0.0195	19.7
Urea	0.2000	0.0175	8.7
Glycine	0.0999	0.0096	9.6

Substance used in the experiment	Weight of substance taken gram.	Amount oxidized gram.	Percentage amount oxidized
α -Alanine	0.0997	0.0365	36.6
Hippuric acid	0.0483	0.0069	14.2
Sodium urate	0.0420	0.0082	19.6
Sodium tartrate	0.0989	0.0679	31.3
Sodium formate	0.0737	0.01467	19.9
Potassium stearate	—	—	40.0
„ oleate	—	—	31.5
„ palmitate	—	—	36.7
„ oxalate	—	—	29.8
Glycerol	0.2500	0.0450	18.0

Moreover, we have shown that in presence of zinc oxide, ferric and uranium nitrates, which act as photosensitizers, the amount of oxidation of the foregoing substances is greatly accelerated.

It will be interesting to note that the Einstein Law of Photochemical Equivalence has been found to be applicable to the photo-oxidation of glucose, lactose, and alanine by air. The law, however, is not applicable to the photo-oxidation of glycine by air, where about seven molecules react per quantum of light absorbed.

In order to find out whether in presence of sunlight, the carbohydrates and nitrogenous substances are oxidized completely to carbon dioxide, or whether other intermediate products are formed, we have estimated in potash bulbs the amount of carbon dioxide obtained in these oxidations, and we have always observed that there were no intermediate compounds, but that the amount oxidized could be estimated by the carbon dioxide obtained in potash bulbs.

Voit in his note on Pettenkofer's work writes "that the metabolism in the body was not proportional to the combustibility of the substance outside the body, but that protein, which burns with difficulty outside, metabolizes with the greatest ease, then carbohydrates; while fat, which readily burns outside, is the most difficultly combustible in the body". We have carried out comparative experiments on the oxidation of butter, egg white, egg yellow, starch, glucose, cane sugar, and glycogen in sunlight and obtained the following results:

Egg yellow	60.9%	oxidized
Egg white	31.25%	„
Starch	38.2%	„
Butter	31.8%	„
Glucose	13.6%	„
Cane sugar	7.8%	„
Glycogen	7.5%	„

It appears, therefore, that egg yellow is the most easily oxidizable substance in presence of light, and that butter is oxidized more than the sugars, which are the least oxidized.

These results on the oxidation of food materials by air in sunlight appear to be suggestive, and the beneficial influence of light in the treatment of diseases may be due to increased metabolism in light. Sunlight and artificial light have been used with success in the treatment of tuberculosis, pernicious anaemia, rickets, etc. The treatment of disease by radiation has been practised since very early times. Recent years have witnessed a great expansion in light therapy, and at present the provision of lamps and accessories has become quite an industry. It is believed that the rays which are absorbed by the skin exert some special influence, and that the beneficial results are not due merely to a heating effect.

Finsen began in 1893 his pioneering work on light therapy. The main success of this worker was with lupus, a tubercular skin disease very difficult to cure. Over 1100 out of about 1200 cases were greatly improved as a result of the treatment. The next important step in light therapy began in 1903, when Rollier established a sanatorium at Leysin, in Switzerland, for the treatment of tuberculosis by sunshine. Important results were obtained, specially with surgical tuberculosis, and light therapy has now become a part of medical practice. Finsen attributed his success in the light treatment of certain local affections to the action of the ultra-violet part of the spectrum. The use of ultra-violet radiation in general diseases is a more recent development. The success of Rollier's light therapy was attributed to the ultra-violet rays of sunlight at high altitudes. On a clear day the amount of radiation at 6000 feet is roughly one and a half times that reaching the earth at sea level. It is not always necessary to expose a patient to direct sunlight, as there is a sufficient amount of indirect ultra-violet radiation in the diffused light from the blue sky. Light therapy has been more successful in the high Alps than elsewhere, not only because of the large amount of ultra-violet radiation available, but also because the snow absorbs heat rays and reflects ultra-violet rays.

The quartz mercury lamp is very convenient in studying the influence of ultra-violet rays upon the human body in general treatment, and it seems to have been established that ultra-violet light plays the preponderant rôle in light therapy, and its application is constantly increasing.

Two types of lamp are used in the treatment of diseases, the air-cooled "sun lamp" for general application or for the treatment

of large areas, and the water-cooled apparatus for local applications. A modification of the "sun lamp" is equipped with a ring of incandescent lamps surrounding the reflector of the mercury vapour lamp. These give out heat, and tend to counteract the coldness experienced by some persons under treatment, especially when this is protracted. The effect of this form of treatment is more like that of a natural sun bath. It seems likely that the air-cooled lamp is especially adapted to yield a radiation containing a larger proportion of the ultra-violet rays of wavelengths exceeding 3000 Å, whilst the water-cooled lamp gives out an intense radiation, much of the energy of which is in the form of rays of wavelengths less than 3000 Å. To secure more effective action, optical sensitizers may be applied to the surface to be irradiated. These sensitizers may be dilute solutions of eosin or another dye, or calcium chloride solution.

Regarding the influence of light on different individuals, Pacini (*Outline of Ultra-violet Therapy*, Chicago (1923)) states: "Speaking generally, light people respond more promptly than dark; females than males, the young sooner than the old; and the regions usually protected from the light, and of high nervous sensibility".

The fluorescence of the eye lens is excited by rays in the region 3500—4000 Å. No radiation shorter than 3500 Å, or probably 3800 Å, can reach the retina. In old age, because of the yellowing of the media, this limit of visibility is pushed into the most refrangible region of the visible spectrum.

In this connection, the following observations of Bodenstein (*J. Soc. Chem. Ind.* **49**, 139 (1930)) are of interest:

"We know that vision is a photochemical process. In the retina there are the rods and cones arranged side by side. The former are covered by a colouring matter—the visual purple, which is changed by light from purple to yellow. The adaptation of the eye to bright light and to dull light is brought about by a photochemical change in this substance. To account for the power of colour discrimination possessed by the eye, we must turn to the cones. These are uncoloured. Weigert has exposed layers of silver chloride and bromide to monochromatic polarized light, and has found that under certain circumstances the layers become coloured by it, thus changing their absorption. This may occur with the cones. We know that they make colour vision possible, and it may be supposed that the layer of material with which they are covered acts in the same way as Weigert's layers of silver chloride and bromide. When exposed to coloured light, they may change their absorption and absorb it. Thus, if exposed to green

light, they may become coloured green, and give us the sensation of 'green'."

When general irradiation is intended, it is desirable to begin by fractional exposures. A fresh part is exposed at each sitting, and the previously treated portions are exposed for longer periods. Exposure of the whole body at the first sitting may lead to serious troubles.

Ellis and Wells (*The Chemical Action of Ultra-violet Rays*, p. 297 (1925)) have stated: "To ascertain the effect upon the skin, eyes, and general condition, Bach resorted to a heroic test. He applied the ultra-violet light with great intensity upon his own person, without protecting his eyes. An exposure of 30 minutes was given at a distance of 16 to 20 inches from a 3000 candle power lamp. The head and body were treated alternately. After 3 minutes there was a sensation of warmth, and after 10 minutes a burning sensation at the place of exposure. An intense reddening appeared in 2 or 3 hours after the treatment. This discoloration disappeared in 3 days. There was no blistering, but the epidermis became hard and dry and peeled within a week, being replaced by a new epidermis which was elastic and brown. The conjunctiva commenced to redden in about 2 hours after the treatment, being inflamed and painful, but the inflammation disappeared in about 3 days without treatment. Immediately after the treatment and for days thereafter, there was a feeling of freshness and of increased energy. This effect perhaps may be expressed as a case of over-stimulation of a person in good health.

In actual practice the ultra-violet radiation is used either as the principal remedial agent or as an adjunct to other therapeutic measures."

According to L. Hill (*Proc. Roy. Soc. B.* 102, 119 (1927)) sunlight focussed on the skin through a 3 percent solution of quinine sulphate, which absorbs rays of the mercury vapour lamp shorter than 4200 Å, does not produce erythema if the skin is kept cool by running water. The erythema-producing rays appear to be in the ultra-violet. Vita glass and green window glass have the following percentage transparency:

	Thick- ness in mm	Wavelength in Å								
		4046	3655	3342	3131	3022	2967	2893	2804	2655
Green glass window	2.8	87.0	76.6	26.0	0.12	—	0.01	—	—	—
Vita glass (1926 sample)	1.3	91.0	89.1	86.5	66.5	48.1	34.5	18.6	5.3	0.4

L. Hill states that in recent samples of vita glass the transmissive power has been improved. Hill has reported that when exposed for two hours to the midday summer sun, the skin of the abdomen reacted with a slight erythema under green window glass, distinct under vita glass, well-marked under silica or no screen. As silica transmits about 90% of all the ultra-violet radiations, while vita glass lets through about 75% of the rays between 3300 to 3000 Å, and green window glass transmits 25% of the rays 3342 Å, and very little of radiations shorter than 3200 Å (compare Coblenz and Fulton, *Bur. Standard Sci. Paper* 495 (1924)), and since in the sun a slight production of erythema occurs under green window glass, a greater under vita glass, and a still greater under silica, it can be concluded that the erythema-producing rays of the sun lie mainly between 3300—3000 Å. Chance's ultra-violet glass transmits rays of wavelengths longer than 3600 Å, and no erythema results under this.

L. Hill states that when exposed to the sun the average fading of the acetone-methylene-blue actinometer on a number of days was $8\frac{1}{2}$ under silica, $7\frac{1}{2}$ under vita glass, and 4 under green window glass. Hence there appears to be a correspondence between the acetone-methylene-blue fading and the erythema-producing power of the sun's rays.

Hausser and Vahle (*Strahlentherapie* vol. 13, p. 59 (1922)), using the mercury vapour lamp radiations of equal intensities as measured by a thermopile, have found the maximum erythema production to be at 2967 Å. At 3131 Å the erythema production was only 4.5 per cent of that at 2967 Å. While the erythema-producing action of rays of wavelength 3131 Å is relatively weak, the intensity of sunlight in this region is sufficient to be effective. The rays of the sun which activate ergosterol by forming vitamin D, which prevents rickets, lie between 3200 and 2900 Å.

Ultra-violet rays reach us diffusely from the blue sky and bright clouds, as well as direct from the sun. Dorno has shown that the ultra-violet rays diffused from the clear sky at Davos, Switzerland exceed those from the low sun. Taking the diffuse ultra-violet from the sun as 100, that from the direct sun was found by Dorno to be as follows:

Height of sun	Ultra-violet radiation
10°	1.7
20°	12.3
40°	47.6
60°	85.1

In the treatment of tuberculosis and skin diseases, ultra-violet light has proved to be very beneficial, and in many chronic diseases ultra-violet light is generally useful. The following quotation from an "Interim Report on Artificial light and X-ray Therapy by L. D. Cruickshank and E. Watt", (published by the *Scottish Board of Health* 1925) will show that medical men attach great importance to the beneficial effect of light therapy.

"Hitherto where growth has been deficient or function defective we have had resource to material remedies. In ultra-violet radiation a new form of treatment is at command. The extent of its therapeutic uses is as yet unknown, but experimental investigation has shown that its therapeutic properties are in the main limited to conditions of growth or of function that are below normal. For example, it has been found to increase body weight, to increase the rate of growth, to improve the mineral content of the blood, to increase the functional activity of the endocrine glands, to increase the bactericidal power of the blood etc., where these are below normal, but to have no corresponding effect on normal individuals. We found in the course of our inquiry that without exception every patient undergoing light treatment experienced an improvement in his or her general feeling of well being, apart altogether from improvement or otherwise in the disease for which the treatment was being given."

According to Cruickshank and Watt, visible light leads to a dilatation of the cutaneous vessels, stimulating the sweat glands and aiding the relief of deep seated congestion.

The rays of longer wavelength, which suffer less absorption by air and by a liquid, are able to exert their stimulative action at appreciable depths. The rays of shorter wavelength are absorbed by the thinnest layers. This will be evident from the following results of Glitscher and Hasselbach (*Brit. J. Actinotherapy*, I (September 1926)), (compare Browning and Russ (*Proc. Roy. Soc. B* 90 (1917))), who showed that radiations of wavelengths 2960—3800 Å are capable of penetrating a considerable thickness of human skin).

Transmission by Epidermis.

Wavelength in Å	Percentage transmission in		Wavelength in Å	Percentage transmission in	
	0.1 mm thickness	1 mm thickness		0.1 mm thickness	1 mm thickness
4360	59	0.5	3130	30	—
4050	55	0.3	3025	8	—
3660	49	0.08	2990	2	—
3540	42	0.02	2970	0.01	—

What is the mechanism by which the biological action of ultra-violet rays is effected? From the researches on the photo-oxidation of food materials by simply passing air at the ordinary temperature, Palit and Dhar have concluded that the light absorbed by the system accelerates the oxidation of food materials taken into the body, and thus that the metabolism in the animal body is increased, that there is a sense of well being, and that disease is avoided. Sunlight is appreciably transmitted by the epidermis, and by absorption of light the body cells are activated and greater amounts of oxidation of carbohydrates, fats, and proteins take place than in the absence of sunlight. It seems generally accepted that several diseases are caused by defective metabolism, and in these diseases sunlight should be efficacious.

Dhar (*Chemie der Zelle und Gewebe* **12**, 217, 225, 317 (1925); **13**, 209 (1926)) has emphasized the importance of sunlight in the treatment of deficiency diseases, because sunlight is transmitted to a greater extent by the epidermis than ultra-violet light, and it seems likely that rickets, osteomalacia, beri-beri, pellagra, etc., would be more common in poor tropical countries like India and China, if the compensating agent, sunlight, were not present.

In this connection, it will be interesting to note that Pincussen (*Biochem. Z.* **150**, 36 (1924)), in his investigation on the effect of solar radiation on the protein metabolism of rabbits, observed a stimulation of the general metabolism, as shown by an increase in nitrogenous excretion. Sensitizers, such as various dyestuffs and potassium iodide, still further increase the nitrogen excretion.

Moreover, we have obtained a marked beneficial effect of sunlight in the treatment of diabetes, which is caused by defective metabolism of glucose; although Sampson (*Physiotherapy Technic*, St. Louis (1923)) thinks that diabetes is not amenable to ultra-violet light therapy, but he admits that this has not been the experience of all others. Bach (*Ultra-violet Light*, New York (1916)) has successfully used ultra-violet light in the treatment of diabetic gangrene.

The lethal effect of ultra-violet radiations is exhibited by the rays shorter than 2900 Å, and the stimulative influence is chiefly exerted by radiations in the region 2900 to 4000 Å. Living beings on the surface of the earth have adapted themselves to exposure to rays of wavelengths not shorter than 2900 Å.

Ellis and Wells (*Chemical Action of Ultra-violet Rays*, page 270 (1925)) have made the following interesting statement regarding the comparative position of light therapy in medical science, "So far from serious burns being caused by ultra-violet rays, exposure to these

very rays is becoming a favourable measure to relieve pain and to promote healing in ordinary burns, in X-ray dermatitis, and in sun burn. Much of the practice in ultra-violet radiation is empirical. This is, however, true of most important advances in therapeutics. Quinine in malaria, mercury in syphilis, iron in chlorosis, ipecac in dysentery, and the majority of our most valuable remedies entered the pharmacopoeia, not through the portals of the pharmacologist's laboratory, but in consequence of accidental discoveries, of lucky guesses, and not infrequently with credentials endorsed by alchemists, astrologers, magicians, and the medicine men of savage races."

PHOTOSYNTHESIS OF VITAMINS.

Huldschinsky (*Deutsche Med. Woch.* **45**, 712 (1919)) proved that infantile rickets could be cured by ultra-violet radiation from a quartz mercury lamp. Hess and Unger (*Amer. J. Dis. Children* **22**, 186 (1921)) correlated the seasonal variation in the occurrence of rickets with the change in the intensity of sunlight.

Fairhall (*Amer. J. Physiol.* **84**, 378 (1928)) has shown that on a normal diet irradiated rats had a somewhat higher concentration of calcium in the serum than did normal rats of the same age. Irradiation increased calcification in rats both on a normal and on a calcium-poor diet.

Hess and collaborators (*J. Amer. Med. Assoc.* **74**, 217 (1920); **77**, 39 (1921)) discovered that rats fed on a diet deficient in vitamins A and D do not develop rickets if they have access to light, and in a preliminary note on the cure of rickets by sunlight, they stated "... encouraged by our results in curing rickets by ultra-violet ray ...". It soon became clear from the researches of Powers, Park, Shipley, McCollum, and Miss Simmonds (*Proc. Soc. Exp. Biol. Med.* **19**, 120 (1921)), and Miss Hume (*Lancet* **2**, 1318 (1922)) on the influence of radiation from a quartz mercury vapour lamp on the prevention of rickets of rats, that ultra-violet light could replace cod liver oil in the prevention of rickets, but that it could not function as the growth-promoting substance, and cannot stop eye troubles. In other words, light appears to act as a substitute for vitamin D and not for vitamin A. Moreover, Pappenheimer and Weinstock (*Proc. Soc. Exp. Biol. Med.* **20**, 14 (1922)) concluded that the effective rays in the cure of rickets were in the neighbourhood of 3130 Å. Hess and Unger (*J. Amer. Med. Assoc.* **78**, 1596 (1922)) used a carbon arc in the prevention of rickets.

Subsequently, Miss Hume and Smith (*Biochem. J.* **17**, 304 (1923); **18**, 1334 (1924)) observed that rats kept in glass jars which were exposed to a quartz lamp for 10 seconds on alternate days kept normal health and growth longer than control rats fed on a diet deficient in the same factors. Almost simultaneously, Steenböck and Black at Maddison University, Wisconsin (*J. Biol. Chem.* **61**, 405 (1924)), and Steenböck and Nelson (*ibid.* **62**, 209 (1924)) discovered that various food materials, and specially those fats which ordinarily do not confer any protection against rickets, became antirachitic on exposure to ultra-violet rays. Steenböck and Daniels (*J. Amer. Med. Assoc.* **84**, 15, 1093 (1925)) concluded that the sterols in food become activated on exposure to light, and this explains the wide range of materials which can be activated (wheat, rolled oats, corn, hominy, starch foods, meat milk, egg yolk, and vegetable oils). Cotton seed and linseed oils become anti-rachitic if exposed for two minutes in thin layers at a distance of one foot from the mercury lamp.

Materials tested for vitamin D potency after irradiation.

Positive.	Negative.
Lettuce (green or yellow) Vegetable oil, sawdust, wheat, cholesterol, phytosterol	Mineral oil, gelatin, air, water, blood serum, chlorophyll, haemoglobin.

Hence several workers concluded that vitamin D or an allied substance is generated from some substance which is common to many naturally occurring food materials.

Shortly afterwards Drummond (*Chemistry and Industry* 994 (Dec. 1926)) observed that by hydrolyzing cod liver oil, which is rich in vitamins A and D, by means of a boiling solution of caustic alkali in absence of air, the full vitamin content was concentrated in the unsaponifiable fraction, which represented about 1 per cent of the original oil, and that all the cholesterol could be removed without affecting the vitamin activity of the residual red brown oil, which is 0.4% of the original cod liver oil. This indicated that the vitamins resembled cholesterol in chemical nature, but that cholesterol itself was inactive. A further discovery was made showing that when cholesterol obtained from brain and rigorously purified is subjected to irradiation, this previously inactive material becomes antirachitic.

Considerable light was thrown on this question by the measurement of absorption spectra. Hess and Weinstock (*J. Biol. Chem.* **64**, 193 (1925)) observed that when cholesterol was irradiated by ultra-violet

light, the activated material showed less absorption of radiations of certain wavelengths than did ordinary cholesterol. The difference in the absorption over an entire range of wavelengths was detected by use of a thermopile and galvanometer. Schultz and Ziegler (*J. Biol. Chem.* **69**, 415 (1926)) observed that carefully re-crystallized cholesterol melting at 148.5° showed selective absorption of wavelengths between 2940—2960 Å and 2790—2940 Å, with general absorption beyond 2940 Å. Heilbron, Kamm and Morton (*Biochem. J.* **21**, 78 (1927)) have verified the work of Schultz and Ziegler, but by fractional crystallisation of cholesterol from ethyl acetate established that ordinary cholesterol contained another compound in small amount, and that this substance, showing a selective absorption about four times as great as the original cholesterol, could be concentrated in the least soluble fraction. This product when illuminated showed an antirachitic activity 3 to 4 times greater than that of an ordinary sample when irradiated. This substance shows three absorption bands with maxima at 2935 Å, 2815 Å and 2700 Å. On illumination, the product becomes antirachitic but the absorption bands disappear.

Pohl (*Nach. Ges. Wiss. Göttingen* (1926)) independently came to the same conclusions as Heilbron, Kamm, and Morton. Hence it appears that the substance existing in small amount in ordinary cholesterol becomes converted into vitamin D on illumination. The nature of this substance, which has been named provitamin D, has been investigated by Rosenheim and Webster (*Biochem. J.* **21**, 127 (1927)), and Windaus and Hess (*Nach. Ges. Wiss. Göttingen* (1927)) and Pohl, working in collaboration. These investigators found that ergosterol, a sterol derived from ergot of rye and from yeast, showed the three absorption bands with intensity, and that on illumination by a quartz mercury lamp the absorption bands disappeared and the substance formed showed great antirachitic properties. Hence it was concluded that provitamin D is either ergosterol or a similar substance.

Morton, Heilbron, and Kamm (*J. Chem. Soc.* 2000 (1927)) examined the absorption spectra of ergosterol, before and after illumination, for different intervals of time, and observed that after illumination lasting for about 150 minutes the absorption in the region 2600 to 3000 Å disappears, but absorption in the region 2300—2600 Å with a maximum at 2470 Å appears. This new band itself disappears on further irradiation, and after six hours all traces of selective absorption completely disappear. It is well known that cod liver oil on long irradiation loses its antirachitic power. Morton, Heilbron, and Kamm concluded from their experiments that the whole of the incident

energy is absorbed by ergosterol and becomes photochemically effective. Rosenheim and Webster state that "the action of ultra-violet light on ergosterol leads to an obvious physical change, and the production of a yellowish resin. The nature of the intramolecular change which gives rise to the vitamin formation is at present unknown. The first step towards solving this problem is the preparation of pure vitamin D, and at present the line of attack most clearly indicated is the prevention of the photochemical decomposition by suitable screening." From an industrial point of view this is an interesting problem. If a satisfactory yield in the reaction: Ergosterol + (ultra-violet light) \rightarrow vitamin D is desired, a prolonged exposure to ultra-violet light screened by "vita glass", which cuts off radiations shorter than 2750 Å, is necessary, and this is an expensive proposition; compare Jendrassik and Kemenyfi (*Biochem. Z.* **189**, 180 (1927)); Rosenheim and Webster (*Lancet II.* 622 (1927)); Heilbron, Kamm, and Morton (*Nature* **120**, 617 (1927)); Heilbron, Morton and Sexton (*J. Chem. Soc.* **47** (1928)); Heilbron and Sexton (*ibid.* 921 (1929)).

Irradiated ergosterol preparations show a curative effect on rickets in young rats in doses of $\frac{1}{100,000}$ mgrm. daily, and with children 0.5 to 1 mgrm. daily. When the mercury vapour arc is used, maximum activation has been reached in 30 minutes' exposure, but the time depends on the experimental conditions; then for a short time the activity remains constant and finally decreases on further exposure. Similar results are obtained by exposing alcoholic or glycerol solutions of ergosterol to sunlight.

Webster and Bourdillon (*Biochem. J.* **22**, 1223 (1928)) have reported that ergosterol shows an increased absorption which runs parallel to the activation in the first stages, and that when the activity decreases there is also a fall of the absorption. The generation of the activity appears to be associated with the formation of an absorption band having a maximum between 2800 to 2900 Å. This is likely to be a property of the vitamin itself, and the destruction of the activity is related to the disappearance of this band and the appearance of another with a maximum at 2300 Å. This band may be the same as that observed by Heilbron, Kamm, and Morton (*Biochem. J.* **21**, 1279 (1927)) in irradiated ergosterol, and believed by them to be characteristic of the vitamin (compare "Ultra-violet Light and Vitamin D in Nutrition", by Miss Blunt and Miss Cowan, *Chicago University Press*).

Heilbron, Kamm, and Morton (*Biochem. J.* **21**, 1279 (1927)) examined spectroscopically a large number of oils, and observed well defined ergosterol absorption bands in some of them.

Kon, Daniels, and Steenböck (*J. Amer. Chem. Soc.* **50**, 2573 (1928)); compare Kon (*Rocz. Chem.* **8**, 502 (1928)), have shown that cholesterol purified by fractional oxidation with permanganate in acetone cannot be activated antirachitically by irradiation. For the photochemical formation of vitamin D from ergosterol, the minimum amount of radiation necessary to produce sufficient vitamin to cause deposit of calcium in the bones of a rachitic rat is 700—1000 ergs, corresponding to the formation of 6×10^{-8} grm. of vitamin D. For monochromatic light from the mercury lines 2560 Å, 2650 Å, 2800 Å, and 2930 Å, the quantum efficiency is independent of the wavelength, and of the continuous or intermittent nature of the irradiation. The same value is obtained with ergosterol, solid or in alcoholic solution, and with ergosteryl acetate. The quantum efficiency of ordinary cholesterol is variable, and may be nearly as high as that of ergosterol.

Recently, Reerink and van Wijk (*Proc. K. Akad. Wetensch. Amsterdam* **32**, 845 (1929)) have stated that the two wavelength ranges 3000—2700 Å and about 2500 Å have different actions on ergosterol. The absorption curves of ergosterol after long irradiation cannot be calculated from those of ergosterol and vitamin D, in consequence of a photochemical change in the reaction product. With short wave irradiation, it is impossible to obtain more than a 15% yield of vitamin D, since there are formed by-products, which produce a maximum in the absorption spectrum with an absorption coefficient of about twice that of ergosterol. As the reaction proceeds the absorption falls to almost zero with the destruction of vitamin D, which has been obtained as lozenge-shaped transparent plates, melting at 0°, by the precipitation of unchanged ergosterol by digitonin.

Pohl (*Nach. Ges. Wiss. Göttingen* **142**, 185 (1926)) has shown that the absorption coefficient at 2800 Å of cholesterol is reduced by half on irradiation, whereas analysis shows that at least 99.5% of the original cholesterol remains unaffected. Hence the bands which disappear must be due to an impurity, which in small concentrations absorbs in the ultra-violet to an extent corresponding with that of ordinary dyes in the visible part of the spectrum.

According to Pohl, the ultra-violet absorption spectrum of ergosterol is essentially coincident with that of the provitamin, which is present in cholesterol to the extent of about 0.017%.

Heilbron, Morton, and Sexton (*J. Chem. Soc.* **47** (1928)) have studied the absorption spectra of a number of cholesterol derivatives, with the object of determining the class of compound to which vitamin D may be assigned. Selective absorption occurs only when at least

two double linkings are present in the molecule. It is shown that the absorption spectrum of cholesterilene resembles that of ergosterol, and it seems probable that two of the three double linkings in the latter compound occupy the same positions as in cholesterilene. Cholestenone and vitamin D also appear to be correlated.

Beck (*Chem. Zentr.* I 2396 (1927)) has shown that irradiation of cod liver oil and milk produces an extension of the absorption spectrum towards the ultra-violet, and that of paraffin oil a contraction.

Bills, Honeywell, and Cox, jun. (*J. Biol. Chem.* **80**, 557 (1928)) have subjected samples of carefully purified ergosterol in alcoholic solution to ultra-violet radiation, and examined the products spectrophotometrically and by biological test. The maximum physiological activity was attained before the absorption curve showed any significant alteration. With increasing length of exposure, the activity decreased and the band at 2480 Å appeared, and the latter band reached its maximum intensity coincidently with the disappearance of physiological activity, and appeared to be associated with the destruction rather than the formation of vitamin D. The freer the access of oxygen, the more rapid is the development and subsequent fading of the band at 2480 Å; such a band, showing similar behaviour on irradiation, is observed in the spectrum of isoergosterol.

Quite recently Rosenheim and Adam (*Proc. Roy. Soc. B.* **105**, 422 (1929)) have suggested from an examination of the surface films of ergosterol and its derivatives that vitamin D may be an unsaturated ketone. The following observations of Drummond (*J. Soc. Chem. Ind.* **49**, 6 T (1930)) will be found interesting: "It is important to remember that the characteristic band of isoergosterol is a little below 2500 Å, and that it has been suggested that the product formed during the radiation and showing a band in this place possesses a molecular configuration similar to that of isoergosterol. If this should be confirmed, it is apparent that the change of ergosterol to vitamin D is not a profound one, as was thought soon after the initial discovery was made, but a relatively slight alteration of the molecule. Isoergosterol, however, is not activated by treatment with ultra-violet light. Another isomeric form of ergosterol, prepared by the distillation of the pinacol and named *neoergosterol*, is also not activated by ultra-violet light. Ergosterol peroxide is not activated. The closely related naturally occurring sterols, zymosterol from yeast and fungisterol from ergot, also fail to serve as precursors of the vitamin. Activation of the esters of ergosterol has been observed. All this evidence suggests that ergosterol is the specific parent substance of vitamin D. Further-

more, a recent examination of the colour reactions and absorption spectra of sterols in relation to their structure by Heilbron and Spring (*J. Soc. Chem. Ind.* **47**, 1113 (1928)) tends to support this view."

It should be emphasized that the activation from the view point of vitamin D, of substances like lettuce (green or yellow), sawdust, wheat, rolled oats, corn, hominy, starch foods, etc. remains unexplained from the foregoing researches.

Orr, Henderson, and Crichton (*Trans. Highland and Agric. Soc. Scotland* (1926)) observed that when pigs nine weeks old were subjected to light treatment from a carbon arc at a distance of three feet for one hour daily, the amount of calcium and phosphorus which the pigs were able to retain in their body was markedly increased, and the amounts excreted in the faeces were correspondingly diminished. Irradiation improves the leg strength of young chickens. Hughes and Payne (*J. Biol. Chem.* **66**, 595 (1925)) and Hart, Steenböck, and Elvejem (*ibid.* **62**, 117 (1924)) have shown that ultra-violet light increases the egg production and improves the quality of eggs of hens. Orr, Henderson, and Crichton state: "It is suggested that there should be a fuller utilization of sunshine for farm animals, and the employment of artificial means of irradiation in winter is put forward as worthy of trial. The agriculturist should realise that the beneficial influence of sunshine falls not alone upon his crop but on all farm animals."

Lillie and Baskerville (*Amer. J. Physiol.* **61**, 57 (1922)) have observed partial activation in unfertilized eggs produced by a short exposure to ultra-violet radiations. Ellis and Wells (*Chemical Action of Ultra-violet Rays*, pages 285—287 (1925)) have described the conclusions of Prof. H. W. Popp from his experiments on the influence of light on the germination and early growth of plants in the following terms:

"Exposures of dry seeds to the full ultra-violet light of a quartz mercury vapour arc have little or no effect on later germination and growth even after 188 hours exposure."

"Exposures of less than two hours duration on soaked seeds that have not yet begun to sprout do not have a marked effect on germination. Longer exposures to the open arc decrease the rate and the amount of germination, inhibit growth and development and finally cause death of the plants. The wavelengths below 3000 Å are more effective in this respect than are those above 3000 Å."

When plants were grown in sunlight from which all wavelengths between 5290 and 4720 Å were eliminated, normal development did not take place. When only the ultra-violet part of sunlight was removed, the plants grew practically in the same way as the controls

in the total sunlight. The experiments of Popp showed that the blue violet end of the spectrum is necessary for the normal and healthy growth of plants, and in general the quality (wavelength) and not the intensity of light is of considerable importance in the growth of plants.

Tsuiji (*Louisiana Planter* **60**, 413 (1918)) has investigated the influence of ultra-violet light in the sugar cane, pine apple and banana industries, and has noted a stimulation in the growth of sugar cane and an increase in the percentage of sugar. Maquenne and Demoussy (*Compt. rend.* **149**, 756 (1909)) have reported that when ultra-violet rays are applied in a proper manner, growth of flowers and vegetation is enhanced.

Sheard and Higgins (*Science* **65**, 282 (1927)) have shown that radiations in the region 3200—3900 Å help, whilst radiations of wavelengths 2700 to 3200 Å from a quartz mercury vapour lamp retard the germination and subsequent growth of seeds. The region 2700—3200 Å, though effective therapeutically, appears to be harmful in the growth of seeds.

Substance	Amount taken in c.c. or grm.	Amount of N/100 thiosulphate required for the iodine in c.c.
Olive oil (<i>Olea Europaea</i>)	3 c.c.	3.20
Mustard oil (<i>Brassica campestris</i>)	3 "	1.40
Cocoanut oil (<i>Cocos nucifera</i>)	3 "	1.00
Mahua oil (<i>Bassia latifolia</i>)	3 "	1.20
Castor oil (<i>Ricinus communis</i>)	3 "	0.95
Til oil (<i>Sesamum indicum</i>)	3 "	1.20
Linseed oil (<i>Linum usitissimum</i>)	3 "	0.90
Butter	0.92 grm.	2.25
Starch	0.10 "	0.20
Glycogen	0.10 "	0.05
Dextrin	0.10 "	0.45
Glucose	0.10 "	0.05

In the foregoing pages it has been shown that numerous workers have concluded that vitamin D or an allied substance is formed when ergosterol is irradiated by ultra-violet radiations. The activation of other edible substances on irradiation has not yet been properly explained. Recently we (Chakravarti and Dhar, *Indian J. Med. Research* **17**, 430 (1929)) have advanced the view that when substances like cholesterol, olive oil, etc. are exposed to light in presence of air, peroxides

are formed, and that these induce the oxidation of food materials mixed with them. Hence the beneficial properties of substances not containing the necessary vitamins are due to the presence of peroxides which help the oxidation of the food materials in the body. The following observations are in support of the above view:

A current of air free from carbon dioxide was passed through solutions or suspensions of the following substances exposed to sunlight for 5 hours. After exposure, an excess of potassium iodide and acid were added to the mixture, and the liberated iodine was titrated with N/100 thiosulphate (see table on p. 468).

The irradiated substances had the property of oxidizing others when mixed with them. The extent to which they oxidized glucose was carefully determined, and some of the results are recorded below:

	% of glucose oxidized
Mustard oil	5.5
Cocoonut oil	3.7
Mahua oil	3.3
Castor oil	4.1
Til oil	2.3
Linseed oil	0.8

From the foregoing observations it is clear that when the food materials are exposed to sunlight in presence of air, they take up oxygen probably forming some peroxide type of compound, which can oxidize other food materials when mixed with them. Consequently the addition of the exposed substances to ordinary foodstuffs facilitates the proper assimilation of food materials, and produces efficacious results.

Moreover, we have carried out feeding experiments with pigeons and we have drawn the following conclusions:

Pigeons do not get polyneuritis in 5 weeks when fed on Rangoon rice alone provided they get sunlight. Leafy vegetables like palak (*pinacia oleracea*), bathua (*chenopodium album*), and tomatoes (substances containing vitamins) when mixed with polished rice appear less effective than sunlight in the prevention of polyneuritis and eye troubles. Colloidal ferric hydroxide and ferric chloride in very small doses are as effective as the above vegetables. Comparative experiments show that sunlight is the best preventive of diseases like polyneuritis and beri-beri. Olive oil exposed to light in presence of air comes a close second, whereas unexposed oils are harmful. In tropical countries many deficiency diseases are prevented by sunlight.

(Compare Chakravarti and Dhar, *Indian J. Med. Research* **17**, 430 (1929)).

It will be interesting to note in this connection that Delore (*Bull. Soc. Chim. biol.* **11**, 74 (1929)) has observed a gain in weight owing to absorption of oxygen, when olive, linseed, and specially cod-liver oils are exposed to air in absence of light. Preliminary irradiation of the oils by ultra-violet light enhances the rate of auto-oxidation up to a limit beyond which it is decreased. In comparison with other oils, cod-liver oil seems to behave as if it had been already irradiated.

Bowen and Tietz (*J. Chem. Soc.* 234 (1930)) have stated that a peroxide is formed when gaseous, liquid, or dissolved acetaldehyde is exposed in presence of oxygen to ultra-violet light. In the liquid and the dissolved states the peroxide is also formed in the dark. The velocity of the reaction is proportional to the square root of the light intensity and the aldehyde concentration, but independent of the oxygen concentration. Alcohol acts as an inhibitor when added to hexane solutions of aldehyde, and the velocity in this case becomes directly proportional to the light intensity.

Recently, Rousseau (*Compt. rend.* **189**, 37 (1929)) has shown that 0.5% of ergosterol dissolved in olive oil and alcohol has a greater power of oxidation when exposed to sunlight in presence of air than cholesterol under the same conditions.

Cluzet and Kofman (*Compt. rend.* **189**, 45 (1929)) have reported that sterols exposed to ultra-violet light, X-rays, or radium rays, blacken a photographic plate. Similarly, Hugounenq and Couture (*Compt. rend.* **189**, 47 (1929)) have shown that indole, skatole, and the sterols of cod-liver oil, *bombyx* and beer yeast darken a photographic plate in direct contact after exposure to ordinary diffused daylight; whilst cholesteryl acetate and sterols of the oils, egg, fresh or red herring, ergot of rye, snail, cow's blood and brain, and biliary calculus are inactive.

Steigmann (*Z. wiss. Phot.* **26**, 363 (1929)) has observed a new photo-reaction with ergosterol, and has shown that alcoholic anthraquinone dissolved in pyridine bleaches alcoholic methylene blue on exposure to light. Shaking with oxygen brings back the colour. Quinone acts in a similar way, but not quinol. When ergosterol, which is a secondary alcohol, was used instead of ethyl alcohol in the reaction, being dissolved in pyridine, the methylene blue was rapidly bleached. Experiments with cholesterol showed that the bleaching in this case is slower than with ergosterol.

ACTION OF LIGHT ON ENZYMES AND ANTIBODIES.

Some interesting work has been carried out on the action of light on enzymes and antibodies and blood. Agulhon (*Compt. rend.* **153**, 979 (1911)) divided the ordinary enzymes into three classes on the basis of their sensitiveness to light:

(a) Enzymes oxidized by air in presence of light of all wavelengths, but destroyed in a vacuum only by ultra-violet radiations — sucrase, tyrosinase, laccase.

(b) Enzymes destroyed by all radiations with or without oxygen — emulsin, catalase.

(c) Enzyme destroyed in a vacuum by ultra-violet light, and somewhat weakened by visible rays — rennet.

Pincussen and collaborators (*Biochem. Z.* **134**, 459 (1923); **144**, 366 (1924); **152**, 406, 416 (1924)) reported that diastase of all concentrations loses its activity on exposure to ultra-violet light, but not in sunlight. They observed that sodium chloride protects diastase and maltase in malt diastase from destruction on exposure to sunlight. Other salts also exert protecting action. The actions of pancreatic, salivary, and takadiastases are increased, whilst that of malt diastase on soluble starch in presence of potassium iodide is retarded by ultra-violet light. These authors showed that the active enzyme in urease solutions is enfeebled in sunlight and destroyed in ultra-violet radiations. Lüers and Lorinser (*Biochem. Z.* **144**, 212 (1924)) compared the inactivation of malt amylase by heat with that by ultra-violet radiation. The ultra-violet light inactivation does not follow the mono- or bimolecular equation, nor the Schütz law. The temperature coefficient ($K_{30^\circ}/K_{20^\circ}$) for the ultra-violet light inactivation is 1.30. Lüers and Lorinser conclude that the two methods of inactivation are different.

Seligsohn (*Biochem. Z.* **168**, 457 (1926)) has reported that blood catalase is more active in dilute than in strong solutions, but is destroyed more quickly by irradiation in the former than in the latter. Similarly, at the optimum p_H (6.81), it is destroyed most rapidly by irradiation.

Pincussen (*Biochem. Z.* **171**, 1 (1926)) has observed that diastase which has been rendered almost inactive by exposure to ultra-violet light is partly reactivated by the addition of a small quantity of non-irradiated diastase.

Pincussen and collaborators (*Biochem. Z.* **195**, 79, 87, 96 (1928)) have investigated the influence of heat and light on salivary, malt, and takadiastase. Potassium, whilst increasing harm by the action

of light, decreases injury by heat, and the reverse is true of calcium. The greatest injury to the action of pepsin, when reacting with fibrin from the blood of different animals in various buffer solutions, on irradiation with ultra-violet light, occurs at p_H 1.14. The lipase action of the serum of rabbits is considerably injured by irradiation.

Kambayashi (*Biochem. Z.* **203**, 334 (1928)) has studied the action of light on takadiastase in presence of sensitizers like eosin, sodium anthraquinone disulphonate, etc. Dilute enzyme solutions are more strongly inactivated than concentrated. Injury to the purified enzyme by light is never greater, and is often less, in presence than in absence of sensitizers.

Bunker and Anderson (*J. Biol. Chem.* **77**, 473 (1928)) obtained no evidence of the acceleration of the enzymic hydrolysis of starch by illumination with polarized light.

Zółciński (*Chem. Zentr.* **96**, I, 1123 (1925); **99**, I, 2443 (1928)) has concluded that chemical nitrification of ammoniacal solutions of natural or artificial humus substances can take place in sunlight but not in the dark, and that the process is more rapid in quartz vessels than in glass vessels. The nitrate disappears in the dark. No nitrification takes place in colloidal solutions. Natural humus undergoes nitrification more slowly than artificial; the change is accelerated by ignited alumina.

Albela (*Deutsche Med. Wochenschr.* **48**, 1347 (1922)) could not detect any change in the phagocytic action with rabbits exposed to ultra-violet rays for long periods. Heuer and Potthoff (*Centr. Bakt. Parasitenk. I. Abt.* **88**, 299 (1922)) observed that the exposure of animals to ultra-violet rays has only a slight influence on the formation of antibodies. Pigmented animals show this influence more than unpigmented ones.

Heuer (*ibid.* **88**, 380 (1922)) states that agglutinins for cholera and paratyphoid A are less resistant to ultra-violet radiations than those of typhoid, and the bacteriolysins less resistant than the agglutinins. Friedberger and Scimone (*Z. Immunitätsf.* **37**, 341 (1923)) have stated that a decrease in amboceptor is observed when hemolytic serum is exposed to ultra-violet rays. Trypanosomes lose their infectivity much sooner than motility on irradiation. Wassermann serums and Sachs-Georgi positive serums of man and rabbits, on illumination with ultra-violet light, become negative.

Balderrey and Barkus (*Amer. Rev. Tuberculosis* **9**, 107 (1924)) observed an alkalinity of the blood when the human body was exposed to sunlight. Frenkel-Tissot (*Deutsches Arch. Klin. Med.* **133**, 286

(1920)) has observed that healthy people in the mountains show the same amount of blood sugar as on the plains.

Koopmann (*Deutsche Med. Wochenschr.* **50**, 277 (1924)) has reported that the concentration of erythrocytes, hæmoglobin, viscosity, and coagulation point of human blood, remain unchanged on illumination of the persons with ultra-violet rays. According to Clark (compare Pacini, "*Outline of Ultra-violet Therapy*" 36 (1923)), radiations of wavelengths 4000—3000 Å cause a reduction in the number of white corpuscles, whilst light of wavelength 3000—2000 Å increases the white corpuscles of lymphatic origin. Kroetz (*Biochem. Z.* **151**, 449 (1924)) has stated that in most patients the water content of the serum increases after irradiation with ultra-violet or X-rays, but becomes normal again after 24 hours.

Recently, Risler, Philibert and Courtier (*Compt. rend.* **186**, 1152 (1928)) have described the great bactericidal action of the light produced by the electric volatilization of aluminium wire. They have shown that *B. tuberculosis* is partly destroyed by the light of the neon lamp in the presence of many dyes, especially those of the pinacyanol class.

PHOTOSTERILIZATION.

It has been known for nearly half a century that ultra-violet radiations have bactericidal properties, and a good deal of work has been carried out in this direction. The following general results have been obtained:

(a) Ultra-violet radiations of wavelengths 2970—2100 Å are most active in killing bacteria, ultra-violet radiations of wavelengths 3800 to 3000 Å have no marked germicidal action, but have greater penetrating power through human skin than radiations of wavelengths 2970 to 2100 Å.

(b) The active rays are those which are absorbed by the substance acted upon, and the total light effect is a function of the intensity of the radiation and the time during which it reacts.

(c) The action is exerted mainly on the protein constituents of the organisms, and possibly the aromatic aminoacids are chiefly attacked.

(d) The penetration of the active rays is feeble, and the turbidity of a liquid greatly obstructs the sterilizing action.

(e) The action of the radiations on the bacteria is a direct one, and is not due to the formation of hydrogen peroxide, ozone, or other germicidal substance.

(f) Atmospheric oxygen is not necessary for the germicidal action of light.

Wide variations have been observed in the photosensitivity of different kinds of bacteria. It has been found that under standard conditions, *Sp. cholerae*, *B. typhosus*, *B. dysenteriae*, *B. coli* are very readily destroyed, and *B. anthracis* (sporogenous), *pneumobacillus*, and *sarcina alba* are slightly less readily affected. The following group of organisms are twice as resistant as the first group: *B. tetani*, *B. megatherium*, *B. phleole*, *B. subtilis*, *sarcina lutea*. *Paramecia* require 10 times and yeast 20 times as long as *B. coli* for destruction. This variation of photosensitivity has been practically utilized: e.g. when milk is sterilized by ultra-violet light, it is observed that the harmful bacteria are more affected than the desirable lactic acid bacilli. Moreover, vaccinia virus can be sterilized by ultra-violet light, because the harmful bacteria are much more sensitive to light than the more desirable organisms.

Cernovodeanu, Henri, and Baroni (*Compt. rend.* **151**, 724 (1910)) observed that an emulsion of tuberculosis bacilli was readily sterilized and tuberculin inactivated by ultra-violet light. Other workers observed that the oxidases of milk, the lipolytic ferments of oils, the complement of serum, diphtheria toxin, and the toxin of lamprey serum, are inactivated by ultra-violet light.

Coblentz and Fulton (*Bureau of Standards, Scientific papers* Nos. **330**, **378** and **495**) exposed atomized suspensions of *B. coli* to ultra-violet radiations from a quartz mercury lamp, and came to the conclusion that the germicidal action of ultra-violet radiations extends up to 3650 Å, decreasing with increasing wavelength. Prolonged exposure is required with radiations from 2970—3650 Å. The lethal action of waves shorter than 2800 Å is about 10 times more rapid than that of radiations greater than 3050 Å, in spite of the much lower intensity of the shorter waves. Coblentz and Fulton calculated that the energy required of wavelengths 1700 to 2800 Å to kill a *B. coli* bacterium is about 19×10^{-12} watt.

In this connection it will be interesting to note that on exposing bacteria which had been sensitized by suspending them in $\frac{1}{5000}$ M aqueous solution of erythrosin, Dreyer observed that the middle region of the visible spectrum, normally harmless, was now lethal. The following table shows the results obtained by Dreyer (Cleaves, *Light energy* p. 190, New York, 1904). — Comparative inefficiency of the longer wavelengths has also been observed with ordinary photochemical reactions.

Filter	Rays acting	Time required to kill bacteria	
		Dyed	Normal
Quartz	Whole spectrum including ultra-violet	60 sec.	60 sec.
Glass	Visible spectrum	10 min.	10 min.
5% Nickel sulphate solution	Red, orange, yellow, green, blue	10 ..	10 ..
Potassium chromate solution	Red to green	15 ..	More than 4 hours
Potassium dichromate solution	Red to yellow	25 ..	More than 9 hours

Although according to Bernard and Morgan (*Brit. Med. Journ.* November 14 (1903)) sterilization *in vivo* by ultra-violet light is an impossibility, subsequent research has shown that in certain types of open wounds, the germicidal action of light can be successfully utilized.

The photosterilization of water has several advantages:

(a) The water itself undergoes no change. The dissolved gases and solids which give to water its pleasing qualities as a drink are almost wholly retained.

(b) Sterilization can be carried to completion and the water can conveniently be utilized for surgical purposes, bottling, washing butter, the margarine industry, and wherever the water is to be added to food.

Turbidity of water has to be removed before ultra-violet sterilization can be effective. Moreover, deposits on the quartz may deteriorate the lamps. Removal of turbidity is effected by sedimentation, or by coarse filtration, with or without the use of coagulants like alum. Greater effectiveness in sterilization is obtained by increasing the amount of short wave ultra-violet radiations from the light source, by rapidly circulating very thin layers of liquid in front of the source of light, and by spraying the liquid.

Regarding the photosterilization of milk, Helbronner and von Recklinghausen (U.S. Patent 1141046, May 15, 1915) have stated that complete sterilization of milk by ultra-violet radiations alone is difficult, and that the prolonged exposure necessary is likely to have harmful effects on the flavour and the digestive qualities of the milk. They propose a combination of heat and ultra-violet ray treatments, and claim that the milk should be heated to 60°, when the flavour is not materially altered but the germs in the milk are so enfeebled that they

are readily destroyed by ultra-violet radiations. It is probable that illumination of the milk results in the formation of vitamin D, but that vitamin A is reduced. If the wavelengths which destroy vitamin A range from 3000 to 3700 Å, it should be possible by suitable light filters to protect the vitamin A, while allowing the germicidal reaction and the formation of vitamin D to continue. Von Recklinghausen (U. S. Patent 1165921, December 28, 1915) recommends the sterilization of opaque liquids by an apparatus which exposes the liquid in a thin film.

Lesure (*J. Pharm. chim.* (VII) 1, 569 (1910)) attempted to sterilize medicinal preparations by ultra-violet rays, especially those used for aseptic injection. Olive, cotton seed, and almond oils can be effectively sterilized by exposure to ultra-violet light for about 3 minutes. The destructive action of ultra-violet light is not only observed with vegetative bacterial cells, but extends to spores and moulds such as penicillium, aspergillus, mucor, etc. Fats and butter spread in a thin layer can be sterilized by ultra-violet radiations. Partial sterilization of barrels, casks, etc. has been effected by lowering quartz lamps into them, and illuminating for about 20 seconds.

Insulin solutions, bacterial vaccines, and other products are also sterilized by ultra-violet light.

A stimulation of the growth of beer yeast exposed to ultra-violet light has been utilized on an industrial scale in the manufacture of beer. Henri, Helbronner, and von Recklinghausen (U. S. Patent 1130400, March 2, 1915) have stated that the taste and colour of fresh wine are changed, and that it soon assumes the characteristics of old wine on exposure to ultra-violet light. This method of ageing wine has been frequently utilized.

CHAPTER XXX.

Practical Applications of Light.

Ultra-violet rays form the basis of numerous interesting processes, such as the deciphering of damaged documents or detecting of frauds in paintings. Ultra-violet light is also being constantly used in important work, such as the testing of dyes and inks for fastness, the artificial weathering of paints and varnishes, the drying of oils, etc.

It has been reported that on exposure to ultra-violet rays, several chemically pure substances exhibit luminescence only faintly, whereas commercial products of an inferior quality show a strong luminescence. Different types of glass exhibit characteristic fluorescence colours. Many substances show notable phosphorescence, for example, rods of fused sodium hydroxide show a reddish white colour in the cone of ultra-violet rays, and a green colour when rapidly moved away. The fluorescence of the eye lens is excited by rays between 3500 Å and 4000 Å.

Testing of dyes. — The application of ultra-violet radiation has been recommended as the most suitable means of determining the light fastness of dyes. Pierce (*Chem. Engr.* **97** (1918)) states that its value and the saving of time resulting from its use are being recognized. The substitution of ultra-violet light for sunlight in the testing of dyes has been opposed on the ground that many dyes vary in their fading by the two methods, and hence that exact comparison is not possible. As the intensity of sunlight and the humidity of the atmosphere vary considerably from day to day, the exposure test in sunlight becomes uncertain. When ultra-violet light is used, the light source, moisture, and time of exposure can be easily controlled, and when a standard substance has been exposed, other dyes may be similarly treated.

Gebhard (*Farben-Z.* **22**, 6 (1911)) uses a cabinet with an enclosed arc or a quartz mercury arc. The change of colour is recorded by orthochromatic photography, using a light filter of the same colour as the original. Gebhard (*Z. angew. Chem.* **23**, 820 (1910)) has advanced the view that the bleaching of dye solutions or of dyed tissues by light in presence of air is due to the primary formation of the peroxide of the dye. Recently, Chakravarti and Dhar (*Z. anorg. Chem.* **142**, 299 (1925))

have shown that the fading of the colours of dyes in visible light is mostly due to photo-oxidation of the dyes by the oxygen of the air, and that in ultra-violet light there is photochemical decomposition of the dyes along with the photo-oxidation. Most of the dyes are unstable substances and they can be reduced or oxidized under different conditions. Along with the quartz mercury vapour lamp, the violet carbon arc, the flame arc, etc. have also been recommended. Harrison (*J. Soc. Dyers and Colourists* **28**, 225 (1912)) and Flynn (*Textile World* **53**, 25 (1923)) have carried out extensive experiments on dyes and fibres with sunlight and the mercury arc lamp. Cellulose has been found to be decomposed by the action of light rays in presence of air, forming reducing agents, and in a vacuum under the influence of the mercury arc cellulose reduces flavanthrene and other dyes. In a vacuum, under the influence of sunlight, cellulose shows slight reducing power. Most colours do not fade in the absence of fibre and air. Basic colours do not fade in absence of air. Under the influence of the mercury vapour light, wool appears to be a less powerful reducing agent than cellulose. Silk and wool appear to have less reducing action than cotton. According to Flynn (*loc. cit.*), direct dyes fade by reduction, which is accelerated by the action of ultra-violet rays on cellulose, whilst basic dyes fade by oxidation.

Heermann (*Chem. Z.* **48**, 813, 834 (1924)) has examined the light-sensitiveness of dyes with different radiations, and has reported that generally the fading of dyed fibres is induced by radiations of wavelengths shorter than 3000 Å; auramine, which is not fast in sunlight, resists short ultra-violet rays fairly well.

Testing of inks. — Rupert (*Ind. Eng. Chem.* **15**, 489 (1923)) has measured the permanence of inks by exposure to sunlight for at least two weeks, and for a shorter period to ultra-violet light. In the testing of inks, the Bureau of Standards (*Circular* 95, June 28, 1920) recommends the exposure of a paper containing streaks of the ink to ultra-violet rays for varying periods up to 48 hours, the relative effects to be recorded.

Drying of oils and varnishes. — The drying of siccative oils is accelerated by light, and the use of ultra-violet light in certain applications of an industrial nature has been proposed. Genthe (*Z. angew. Chem.* **19**, 2090 (1906)) investigated the drying of linseed oil by exposing it (on a filter paper contained in a quartz flask) to ultra-violet light in an atmosphere of oxygen. No ozone was observed. During the first two hours the absorption of oxygen was small. In the third hour the absorption became rapid, and gradually diminished during subsequent hours of exposure.

Schofield (British Patent 227212, October 16, 1923) has described

an apparatus in which the oil, such as linseed oil, is sprayed through a chamber illuminated by a high tension electric discharge, purified and dried air being supplied under pressure and at a temperature of about 250°.

Wolff (*Farben Z.* **24**, 1119, 1389 (1919)), Ragg (*ibid.* **24**, 1308 (1919)), Vollmann (*ibid.* **24**, 1427 (1919)) and Ellis (*Chemical Action of Ultra-violet Light* 319, 1925) have studied the action of light on the drying of varnishes. No definite conclusion can be drawn from their researches. Gardner and Parks (U. S. Paint. Manufact. Assoc. March. 1923, Circular 172) have investigated the influence of ultra-violet and coloured rays on the drying of linseed oil and varnish, and have observed that when sunlight, direct or filtered through different types of coloured glasses, was used as a light source, no appreciable difference in the times of drying of a film of raw linseed oil exposed to air was noted. The film dried at a more greatly accelerated speed in light than in the dark. When diffused daylight is used, different coloured lights produce different rates. When ultra-violet radiations were filtered through red glass, the accelerating effect was lost.

According to Marcusson (*Z. angew. Chem.* **35**, 543 (1922)), drying oils when kept free from air in daylight, or in ultra-violet radiations, undergo polymerization; the iodine value decreases and the specific gravity increases.

Patent leather. — Lumbard (*J. Amer. Leather Chem. Assoc.* **84** (1915)) claimed that in the manufacture of patent leather, when the varnished surfaces are exposed to ultra-violet radiations from a mercury vapour lamp, the same drying effect is obtained in 90 minutes as is obtained by several days' exposure to sunlight. Priest (U. S. Patent 1262977, April 16, 1918) finds that ultra-violet light is a better drying agent than sunlight, after the leather has been coated with the linseed oil varnish mixture. Leather may be subjected to ultra-violet rays before being enamelled or treated.

Durability of paint films. — Nelson and collaborators (*Amer. Soc. Test. Materials* **22**, II, 485 (1922); **23**, II, 356 (1923)) have tested the durability of a series of paints by exposing them to ultra-violet radiations from a mercury vapour lamp for 24 hours, the temperature of the paints being between 50 and 60°. The destructive effect appears to be exerted by radiations in the neighbourhood of 3000 Å. While a certain light-resistant lithopone maintained its whiteness over a period of three years' exposure to air and the atmospheric changes of temperature, humidity, etc., the effect of the ultra-violet light was to discolour lithopone and white lead in a short time. Nelson and Rundle (*loc. cit.*) have noticed that films exposed to ultra-violet rays increase in tensile

strength and decrease in extensibility, but this effect is less pronounced with films containing zinc oxide, which is opaque to ultra-violet radiations, than with films containing white lead, which is more transparent. The hardening and disintegration of a linseed oil binder caused by ultra-violet light led to the failure of paints by chalking.

Pfund (*Proc. Amer. Soc. Testing Materials* **23**, II, 369, 377 (1923)) has tested the reflective powers of dry pigment surfaces by calculation from photographic records. When light falls on a layer of fine particles, it passes through a large number of particles before being reflected, and hence the reflection coefficients are only a qualitative measure of the opacities of the pigments tested. Zinc oxide is practically opaque near 3600 Å, but white lead is the most transparent amongst ordinary pigments. Titanox, timonox, and lithopone lie between zinc oxide on the one hand and white lead on the other. Powdered sulphur is very opaque. Magnesia has constant reflecting power throughout the ultra-violet spectrum. Linseed oil is opaque to wavelengths shorter than 2900 Å. Since ultra-violet radiation causes the deterioration of the oil in paint films, it is desirable that the pigment should absorb the harmful radiations. When lithopone water paste is illuminated by an iron arc spectrum, it is observed that radiations greater than 3200 Å show very little darkening effect. The sensitivity of lithopone is practically zero in the visible spectrum, rises to a high value near the region 2900 Å, and then remains practically constant. The bleaching action of light on a yellow paint film is quite pronounced in the region 3200 Å. Similar results have been obtained by Hallet (*Proc. Amer. Soc. Testing Materials* **23**, II, 379 (1924)), and Gardner and Holdt (U. S. Paint. Manufac. Assoc. Circ. 194, January 1924). Many pigments other than lithopone, even some of the so-called inert pigments, darken or show a slight graying on exposure to ultra-violet rays. The following results of Pfund (*loc. cit.*) on the bleaching of yellow paint films (linseed oil) by sunlight filtered through different screens will be found interesting:

Screens	Wavelength reaching the film Å	Remarks
(1) No screen	2900	Vigorous bleaching
(2) Quartz plate	2900	"
(3) Glass plate	3200	"
(4) Crookes's glass	3600	Bleaching (less than in the previous cases)
(5) Noviol glass (yellow)	4900	Bleaching less than (4)
(6) Ruby glass	6000	No bleaching

Brickwedde (*J. Opt. Soc. Amer.* **14**, 312 (1927)) has shown that lithopone, a white pigment containing about 26% zinc sulphide, darkens on exposure to ultra-violet light; this darkening is due to the formation of metallic zinc and liberation of sulphuretted hydrogen. The sensitivity of lithopone showed a maximum at 3126 Å, and similar measurements on precipitated silver chloride showed an increase in sensitivity at 3650 Å.

During recent years, the mercury vapour lamp has been used extensively for the testing of nitrocellulose lacquers, lacquer enamels, and other varnishes; but Mougey (*Ind. and Eng. Chem.* **17**, 412 (1925)) could not find any direct relationship between the ultra-violet ray tests and service tests when different types of materials were compared.

Treatment of non-drying oils.— Ultra-violet rays have been utilized for the destruction of the objectionable taste and odour of some vegetable oils. Putland (*Cotton Oil Press* **7**, No. 7, 36 (1923)) has noted that light from Mazda lamps is more effective in the bleaching of vegetable oils than sunlight, but ultra-violet light instead of bleaching darkens cotton seed and soyabean oils. The bleaching of oils, fats, waxes, and resins by the joint action of oxygen and ultra-violet light is recommended by Genthe (*J. Soc. Chem. Ind.* **29** 1168 (1910)). The oil or fat or resin is heated to 70°–90°, air is passed and the oil subjected to the action of ultra-violet light from a quartz mercury lamp immersed in the substance which is being bleached.

Ellis (*Chemical Action of Ultra-violet Rays* pp. 328–330, 1925) has investigated the action of ultra-violet light on various oils, resins, etc. in thin layers, regarding their bleaching and polymerization. Cotton seed oil, whale oil, and linseed oil gelatinize on exposure, due to partial oxidation and polymerization. When the gelatinized products are exposed to air for 24 hours, they become opaque and quite brittle. In several cases, on exposure to light and air, the molecular weight of the oils increased considerably, showing polymerization. According to Wierusz-Kowalski (French Patent 468,215, Feb. 5, 1914), oils may be bleached by spraying them into vertical tubes by compressed air or steam, and exposing them to ultra-violet rays.

Oil hardening and testing of hydrogenated oils.—Walter (*Z. angew. Chem.* **27**, 1, 249 (1915)) has worked out a process of hydrogenating oils, in which an oil film on a web carrying the catalyst is exposed to ultra-violet radiation.

Ultra-violet rays have been used for the detection of unhydrogenated oils in hydrogenated oils or fats. Ordinary greases or fats are darkened and polymerized on exposure to ultra-violet light, whilst

hydrogenated and hardened oils are not visibly changed after several hours' exposure.

Custis (*J. Franklin Inst.* **184**, 880 (1917)) did not observe any influence of radiations from an iron arc on the hydrogenation of oleic acid.

Petroleum oils and resins.—Petroleum oils, which are used as lubricants, and which may have sticking properties due to unsaturated constituents, are improved in quality on exposure to ultra-violet radiation, because of polymerization of the unsaturated oils. Gray (U. S. Patent 1,158,205, Oct. 26, 1915) converts 75% of the hydrocarbon materials present in lubricating oils and paraffin wax by blowing air through them at 50°—120° and irradiating by ultra-violet rays. Continental Caoutchouc and Guttapercha Company (French Patent 469,948, March 21, 1914) crack petroleum oils by heating with a catalyst and spraying through a space illuminated by ultra-violet rays.

Ultra-violet rays have been employed for bleaching rosin, and for rendering asphalt more insoluble. A substitute for oils as a medium for paints, varnishes, etc. has been proposed by Rohm (*J. Soc. Chem. Ind.* **36**, 296 (1917)), and it consists of a solution of polymerized acrylic acid ester in acetone or other solvent. When exposed to sunlight or ultra-violet light, the ester is converted into a colourless, transparent, and tough mass, which is soluble in solvents for oils.

Rubber.—Victor Henri in 1909 was the first to use ultra-violet rays in the vulcanization of rubber. Rubber solutions in benzene or xylene, containing sulphur, when spread on a moving metallic ribbon can be vulcanized by exposing them to the action of ultra-violet rays from a quartz mercury vapour lamp for a few seconds. Along with vulcanization in light there is also depolymerization. It is concluded that in absence of air, ultra-violet light activates sulphur into thiozone, and that the vulcanization is effected partly by the latter and partly by the ozone formed simultaneously. One per cent solution of dimethyl amino-methyl coumarin may be used to absorb ultra-violet rays, and hence protect the fabric of balloons against sunlight. Carbon black, used as a reinforcing agent in rubber, prevents the penetration of light, especially ultra-violet, into rubber. The action of ultra-violet rays upon rubber increases the photo-oxidation of rubber.

Paper and Textiles.—The fact that ultra-violet radiations of wavelengths 3300—2100 Å, when projected on to a sheet of a note paper or a piece of bleached cotton fabric, become converted into visible rays, which can be photographed with an ordinary camera, may be utilized in the testing of paper, cotton fibres, fabrics used in automobiles, etc..

When a piece of paper is coated with a mixture of gelatin, casein, or other protein matter, and potassium or sodium bichromate, and exposed to ultra-violet radiations, the protein is rendered insoluble, and the paper is water-proofed and strengthened.

Coarse yarns are less affected by light than fine yarns, because in the coarse ones the outer layers protect the inner ones. Silk is more attacked in presence of light than cotton, but wool is least affected. Artificial silk is affected less than cotton. Ultra-violet rays from a quartz mercury lamp, which weaken silk and artificial silk, are almost entirely cut off by interposing a glass plate, but weakening of cellulose threads by light appears to be due chiefly to rays of wavelengths less than 4000 Å. The nature of these changes is the photo-oxidation of the materials by the oxygen of the air in presence of light. The tearing strength and elasticity of wool are practically unaffected both by sunlight and the rays from a quartz mercury lamp.

Neutral wool develops a rose violet colour when treated with a solution or the vapour of quinone, but a deep brown colour is observed when the wool has been previously exposed to sunlight or ultra-violet rays. This sharp difference of colour has been utilized for making photographic prints on woollen fabric.

When exposed to ultra-violet radiations, parchment fluoresces, but erased writings remain almost dark. Thus, fluorescence photography brings out details, and is useful in the study of old manuscripts. The use of ultra-violet rays in deciphering damaged documents, such as wills, has been recommended, where the chemical and photographic methods and X-rays have failed to decipher them. On exposing the previously heated paper to radiations from a mercury vapour lamp, with a suitable nitroso-dimethylaniline filter, the writing becomes fluorescent, and can be easily read. Frauds in paintings can be detected by exposing the canvas to ultra-violet rays, taking photographs and enlarging them.

Food products.— Ultra-violet light has been used in the detection of shells in cocoa. The colour of the shell tissues, when seen by the ultra-violet rays filtered through a uviol glass cell containing nitroso-dimethylaniline, and another cell containing copper sulphate solution, is buff or brown, and the mucilage cells being yellowish green or colourless, the nib tissues appear in blue violet shades.

Ultra-violet radiation has also been used in the treatment of flour with oxidizing agents. Meal or flour is treated with chlorine to render the enzymes inactive, and then treated with hydrogen peroxide and exposed to ultra-violet rays to liberate oxygen, which acts as a bleach-

ing agent. The colour and baking qualities of meal, flour, cereals, beans, or tubers are improved by the above process.

An important application of ultra-violet radiation is in poultry houses for the prevention of rickets in chickens, and the consequent loss in egg production. A daily exposure for a short time is recommended (see p. 467).

Minerals and metals.—Certain minerals are inert, others fluorescent, and some phosphorescent when exposed to ultra-violet rays. The discovery of the mineral kunzite was made by means of ultra-violet rays. A large number of spodumene specimens were tested and found to be inert except one, when illuminated by ultra-violet rays. On more careful investigation, this one was found to be a hitherto unknown mineral, which was named "kunzite" after the discoverer G. F. Kunz.

The genuineness of diamonds may be proved by their phosphorescence after being subjected to ultra-violet rays. Similarly, a crushed mineral may readily be separated into fluorescent and nonfluorescent portions by sorting while under the action of ultra-violet rays, and this process of separation is being utilized industrially. Hence, in the field of detection of minerals there is plenty of scope for the application of ultra-violet radiations.

Lighting by luminous paints has also been proposed. A surface coated with a luminous paint containing a phosphorescent sulphide is rendered steadily luminous by subjecting it to the rays of the spectrum from blue to ultra-violet. The sulphide can be mixed with a varnish, and the luminous coating covered with a fireproof and impermeable layer consisting of cellulose acetate, alcohol triacetin, or acetone and tetrachloro-ethane.

Industrial photohalogenations.—Chlorination of toluene in light to make benzyl chloride, benzal chloride, and benzotrichloride, and the formation of benzyl alcohol, benzaldehyde, and benzoic acid by the hydrolysis of the halogen derivatives, have received considerable commercial support, and have been in use for a long time. The chlorination of methane in order to obtain chloroform and carbon tetrachloride represents another important step in the industrial halogenation processes. Amyl alcohol is largely used in the production of nitrocellulose coating compositions, but due to wartime necessity and liquor prohibition in America, there was a shortage of amyl alcohol. Extensive attempts to chlorinate butane, pentane, and hexane, to form monochloro-derivatives, which could be converted into the corresponding alcohols or acetates, were made to meet the scarcity of amyl alcohol.

It appears, therefore, that photohalogenation processes are of considerable importance.

According to Mott and Bedford, the light sensitiveness of halogens and their compounds is as follows: Fluorine and its compounds are not sensitive to light; even silver fluoride is quite insensitive to light, although the other halides of silver are highly photosensitive. Sulphur fluoride is not decomposed by light, although oxides and hydrides of sulphur are decomposed by ultra-violet rays. Calcium fluoride is the most transparent substance to ultra-violet radiations known to us, and is extremely stable towards light. It appears that fluoride ions in a crystal lattice show no absorption of rays longer than 1250 Å, and photochemical changes cannot take place unless the cations absorb radiations, and even then photochemical action may not occur. The other halogens react more readily in the light than in the dark. Chlorine is influenced by blue, violet, and ultra-violet radiations, and its absorption spectrum extends further into the ultra-violet, with a maximum at 3380 Å. The photosensitiveness of silver chloride appears to be more marked in the ultra-violet than that of silver bromide. Free bromine is more sensitive to longer wavelengths than chlorine. On the other hand, hydrobromic acid is more easily decomposed by ultra-violet radiation than is hydrochloric acid. The absorption spectrum of iodine extends still further towards the long wavelengths, and hydriodic acid is decomposed by blue and violet light. The absorption spectra of the halogens do not, however, suffice to explain the mechanism of photohalogenation. Owing to the absorption of light the halogen molecules are either atomized or activated, and then react.

We shall now consider the chlorination process of methane devised by Bedford (*J. Ind. Eng. Chem.* **8**, 1090 (1916)) and Mott and Bedford (*ibid.* **8**, 1029 (1916)).

They have observed that one volume of chlorine will react with seven volumes of natural gas when illuminated by the white flaming arc. When the reaction is continued, the speed of the conversion slows down as the residual gas becomes diluted with hydrochloric acid, nitrogen, etc. Natural gas is confined in a bell jar over water through which chlorine is bubbled, and exposed to light from a flame arc. On shaking, the hydrogen chloride formed in the reaction dissolves in the water, and the products, which are liquid at room temperature, are condensed. A large scale experiment in which 30 cubic feet of gas were consumed per hour gave several gallons of liquid products of the following compositions:

	Liquid separating out under water layer in per cent.	Liquid soluble in water and separated by distillation in per cent.
Methylene chloride	35	60
Chloroform	35	28
Carbon tetrachloride	5	1.5
Chloroethanes	20	6

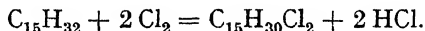
Mott and Bedford (*loc. cit.*) compared the efficiencies of the flame arc and a Heraeus mercury quartz lamp in photochlorination reactions. Chlorine gas was passed into the liquid to be reacted upon until a strong yellow colour was obtained. The liquid was then divided into two equal parts, one part being placed in a cool, dark vessel, while the other part was exposed to one of the lamps. A high concentration of free chlorine in a liquid with which it will react requires comparatively little radiation to start the reaction, and the lower the content of free chlorine the greater is the light energy necessary. The higher the temperature the less is the light energy required for the reaction. From their work Mott and Bedford conclude that a large share of the actinic power of the quartz lamp lies in the ultra-violet rays, which are not required for chlorination processes.

Tompkins (British Patent 780, January 18, 1915) has shown that coal gas rich in ethane is produced by distilling coal at a temperature of 500—600°. The ethane and small quantities of ethylene are separated by liquefaction, and then again gasified and mixed with chlorine and exposed to the radiations from a quartz lamp. The coal gas may also be chlorinated directly, but in this case the amount of the incident light should be smaller than that which would cause appreciable chlorination of the methane present.

In the process of Leiser and Ziffer (U.S. Patent 1,459,777, June 26, 1923) for the production of methyl chloride, a mixture of one volume of methane and six volumes of chlorine is passed rapidly through a series of cooled reaction vessels, and exposed in these vessels to light from a mercury vapour lamp. The addition of small quantities of water vapour and hydrochloric acid retards the formation of products other than methyl chloride, and the separation of carbon. The yield of methyl chloride is about 85%.

In the process for the chlorination of saturated hydrocarbons worked out by Blanc (U.S. Patent 1,248,065, Nov. 27, 1917) light as well as catalysts are used. Brooks, Essex, and Smith (U.S. Patent

1,191,916, July 18, 1916) have described a method of chlorinating liquid hydrocarbons such as benzene, toluene, gasoline, petroleum oils, etc. by exposing the liquids kept at a definite temperature to light from a gas-filled tungsten filament lamp, or mercury vapour lamp, into which chlorine is introduced. If the material to be chlorinated is not a liquid, it may be melted or dissolved in a suitable solvent. In the chlorination of pentane, Brooks, Smith, and Essex (*J. Ind. Eng. Chem.* **10**, 511 (1918)) have observed that when the chlorination is once started by strong ultra-violet light, it can proceed very smoothly in diffused daylight. Brooks and Padgett (U.S. Patent 1,220,821, March 27, 1917) have developed a method for the production of non-volatile unsaturated hydrocarbons from petroleum oils, suitable as non-saponifiable substitutes for linseed oil in paints. For example solar oil is first chlorinated:



The dichloride obtained is then subjected to a temperature ranging from 350° to 550° in the presence of a catalyst, when hydrochloric acid is given off with the formation of unsaturated hydrocarbon.

Boyd (U.S. Patent 1,293,012, Feb. 4, 1919) recommends a continuous system of chlorination to prepare monochloroparaffins. Rodebush (U.S. Patent 1,402,318, Jan. 3, 1922) has described an apparatus for halogenating liquid hydrocarbons, in which the liquid is circulated from the main reaction vessel through a small tube, where it is exposed to radiations from a mercury vapour lamp.

Okimaka and Sakai (Japanese Patent 35,994, 1920) have adopted a vessel for chlorination by ultra-violet rays consisting of a closed chamber provided with a window having a uviole glass or quartz lens, and two tubes opening at the focus of the lens, and another tube for the exit of the product. A chlorinating apparatus, in which the reacting material is illuminated and heated by passing round a source of ultra-violet rays before entering the main reaction chamber, has also been devised by Sakai and Okimaka (Japanese Patent 39,940, Sept. 14, 1921). Halogenated paraffin hydrocarbons have been obtained by Gaul and Hanschke (U.S. Patent 1,032,822, July 16, 1912) by mixing the hydrocarbon and chlorine in the dark, and then exposing the mixture to ultra-violet rays. Eldred and Mersereau (U.S. Patent 1,234,886, July 31, 1917) have observed that olefines, produced by cracking oil, are converted into chlorinated products when treated with chlorine in presence of ultra-violet rays. Snelling (U.S. Patent 1,271,790, 1,285,823, 1,325,214, 1,523,563, January 20, 1925) has

worked out several methods for efficient photochlorination of hydrocarbons in the gaseous condition. In chlorinating methane, ethane, propane, ethylene, etc. a mixture of chlorine and the substance to be chlorinated is passed backwards and forwards between transparent baffle plates. A mercury vapour lamp within the inner dome of the apparatus and the regulation of the reaction temperature control the progress of the chlorination process. By this method Snelling prepared carbon tetrachloride and chloroform. The baffle plates reduce the light intensity and assist the mixing. This method has been extended to the chlorination of liquid hydrocarbons.

Snelling (*J. Soc. Chem. Ind.* **39**, 476 (1920)) has described a photochemical apparatus in which the reacting fluids are made to pass through a series of transparent vessels, each of which has a light source opposite to it; the distance between the light source and the reaction vessel is decreased progressively in the direction of flow of the fluids.

Keyes (U.S. Patent 1,237,652, Aug. 21, 1917) has developed an important method for photohalogenation, in which a quartz mercury vapour lamp of the straight tube type is fitted with a jacketing tube having a condenser, a vent, an inlet, and an outlet tube. This arrangement is suitable for the production of chlorine or bromine derivatives, and is adapted to continuous operation. Lacy (U.S. Patent 1,308,760, 1921) has shown that if methylene chloride, water, and chlorine are introduced into a closed reaction vessel and exposed to ultra-violet light, chloroform and hydrochloric acid are produced.

The chlorination of natural petroleum gas has been studied by Tolloczko (*Chem. Zentr.* **84**, II, 99 (1913)) in the outer coating of an ultra-violet lamp set up in the form of a Liebig condenser. The temperature was varied between 80° and 100°. The volatile portion consisted mainly of methyl chloride and dichloromethane. The oily products were separated by fractional distillation into dichloromethane, carbon tetrachloride, dichloroethane, and tetrachloroethane.

Payne and Montgomery (U.S. Patent 1,453,766, May 1, 1923) have worked out a catalytic photochlorination process. Shale oil or a high boiling paraffin, or other oils mixed with powdered coal, are treated with chlorine at about 150°, and the product formed, which is a black porous solid, is a suitable catalyst for the chlorination of gaseous hydrocarbons. Chlorine and a moist hydrocarbon vapour are led over this catalyst in the proportions of three to one, and the temperature in the reaction vessel is kept at about 150°. The chlorination is completed by passing the products of the reaction through

fused silica tubes exposed to the radiations from a quartz mercury lamp.

The following points are of importance in these various halogenation processes: (1) If the reaction has to be carried on in radiations from a quartz mercury vapour lamp, it is practically useless to employ reaction vessels made of thick glass, because a good deal of the actinic rays will be cut off in this way; (2) stirring devices are essential when liquids are subjected to photochlorination; (3) cooling devices are also necessary in several cases; and (4) the hydrochloric acid formed should be absorbed as quickly as possible.

Volmar (*Bull. Soc. Chim.* IV, **27**, 681 (1920)) has shown that methyl sulphate undergoes chlorination to methyl chloromethyl sulphate at room temperature in presence of light. Both a mercury vapour lamp and a metal filament lamp have been used.

Kling, Florentin, Lassieur, and Schmutz (*Compt. rend.* **169**, 1046 (1919)) have prepared methyl chloroformate by the action of carbonyl chloride on methyl alcohol at as low a temperature as possible. By moderate chlorination in the presence of sunlight, arc light, or the light from an incandescent lamp, the monochloresters are prepared almost free from the dichloresters. Grignard, Rivat, and Urbain (*Compt. rend.* **169**, 1074, 1143 (1919)) have shown that light exerts a marked influence on the chlorination of methylchloroformate. In diffused light, it is only the chloromethyl ester which is formed, bright sunlight being necessary for the formation of the di- or tri-chloromethyl ester, while in ultra-violet rays the trichlor-ester is easily obtained. The chlorination takes place smoothly between 110° — 112° , but at 117° decomposition with the formation of carbonyl chloride takes place.

Discussing the manufacture of "poison gases" in Germany, Carr (*J. Soc. Chem. Ind.* **38**, 468 (1919)) reports that the preparation of diphosgene is a tedious process, which involves the chlorination of methyl formate for a week in presence of light from Osram lamps of 4000 candle power. Custis (*J. Frank. Inst.* **184**, 874 (1917)) has observed that the photochlorination of glacial acetic acid to monochloroacetic acid requires ultra-violet light of considerable intensity, because an iron arc was effective but the light from a projection lantern ineffective.

Book and Eggert (*Z. Elektrochem.* **29**, 521 (1923)) have stated that at a temperature of 105° to 110° , the product of the interaction of chlorine and toluene is largely benzyl chloride in the dark, or in light if catalysts like ferric chloride, iodine monochloride, etc., are excluded. In presence of ferric chloride, ortho- and para-chlortoluenes are

generated. At -80° chlorine and toluene react in presence of visible light, but the quantum yield is much greater than unity; there is no dark reaction at -80° .

Gibbs and Geiger (U.S. Patent 1,246,739, Nov. 13, 1917; Canadian Patent 186,466, Sept. 10, 1918) have studied in detail the chlorination of toluene. When chlorine gas is passed into boiling toluene until a definite weight of chlorine has been absorbed, it leads to the formation of benzyl chloride as the main product, but substances containing chlorine in the ring are also formed. Toluene vapour in presence of an excess of chlorine and a catalyst forms a mixture of benzyl chloride, benzal chloride, benzotrichloride, chlorotoluene, and chlorobenzyl chloride. When the toluene is in excess, the presence of a catalyst with light forms benzyl chloride. The chief point in the patent of Gibbs and Geiger is that in presence of ultra-violet rays, toluene vapour and chlorine gas are assumed to react completely to form chlorinated side chain derivatives. Ellis (U.S. Patent 1,202,040, Oct. 24, 1916) has developed a method specially suitable for the production of benzyl chloride. Selden Company and Gibbs (British Patent 123,341, Oct. 22, 1917) have obtained benzyl chloride and benzal chloride from toluene, by passing a mixture of the hydrocarbon vapour and chlorine gas through a vessel exposed to radiations from a low pressure mercury vapour lamp.

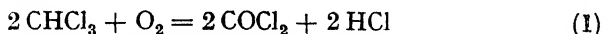
Olivier (*Rec. trav. chim. Pays-Bas*, **36**, 117 (1916)) has shown that when para-chlorobenzene-sulphochloride dissolved in ether is exposed to sunlight, or the radiations from a uviol lamp, chlorine is liberated and oxidation takes place with the formation of sulphonic acid.

Chloroform and carbon tetrachloride are often employed as solvents in photochlorination reactions, and it is desirable to find out how these compounds behave when exposed to light. Chloroform is rather unstable, especially towards ultra-violet light.

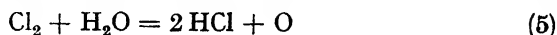
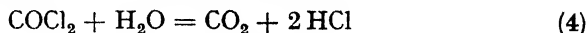
Kailan (*Monatsh.* **38**, 537 (1917)) has made comparative experiments on the influence of ultra-violet rays and radium emanations on chloroform and carbon tetrachloride. Ultra-violet light seems to be more active than radium emanations; chloroform becomes turbid and increases in density. Hydrochloric acid, hexachlorethane, and an amorphous reddish brown solid are detected in the undecomposed chloroform after exposure.

Recently, Chatterji and Dhar (*Z. anorg. u. allgem. Chem.* **191**, 155 (1930)) have investigated the oxidation of chloroform in glass vessels by air at 40° in tropical sunlight, and have shown that hydrochloric acid, chlorine, carbonyl chloride, carbon monoxide, and carbon dioxide are

formed in the reaction. The chemical changes involved in this photo-oxidation can be represented as follows:



In presence of moisture, the following changes also take place:



The reaction (1) has the greatest velocity, and reactions (3) and (5) are slower than (1).

In absence of oxygen, even in tropical sunlight, chloroform decomposes slightly in glass vessels. Quantitative chlorination of chloroform to carbon tetrachloride can be effected by radiations of wavelengths 3000—3400 Å.

According to Benrath and Hertel (*Z. wiss. Phot.* **23**, 30 (1924)), commercial or even ordinarily purified carbon tetrachloride absorbs chlorine. If the material be rigorously purified by being treated with chlorine, nitric acid, and finally sodium carbonate, and then washed, dried, and redistilled, there is no absorption of chlorine, but a slow liberation of chlorine takes place, on exposure to light. Massol and Faucon (*Compt. rend.* **159**, 314 (1914)) have reported that ordinary carbon tetrachloride contains traces of carbon disulphide.

Le Blanc and Andrich (*Z. Elektrochem.* **20**, 543 (1914)) have studied the photobromination of toluene in an atmosphere consisting of 96% oxygen and 4% nitrogen. The yield of benzyl bromide is independent of the light intensity, and is constant throughout the entire spectrum. The velocity of the reaction decreases with the wavelength, and becomes practically zero for wavelengths shorter than 3000 Å. Bromination of toluene in ethyl acetate seems to be unaffected by light. These results seem rather peculiar, and the experiments need confirmation.

Iodine derivatives of paraffins (except methane) may be prepared by mixing the hydrocarbons with iodine in the dark and exposing the mixture to the action of short wave ultra-violet light.

The following lines from the Presidential address of Mr. J. A. Reavell (*Chemistry and Industry*, April 11, 1930, page 307) are of interest:

"With the development of X-rays and ultra-violet rays, another scientific instrument had been placed at the disposal of industry.

X-rays were used in the manufacture of patent leather, the object being to toughen the varnish medium so that it formed a hard bright surface that would remain pliable. The application of this medium was being extended to artists' colours.

"A large number of organic and inorganic substances by absorption of ultra-violet light exhibited characteristic fluorescent colours, which property was made the basis of a simple and rapid method for testing and identifying materials. In the rubber industry ultra-violet rays might be used for checking the purity of zinc oxide, lithopone, oils, accelerators, etc. and for the detection of errors in mixings due to mistakes in the incorporation of the ingredients. Changes such as those produced by natural and artificial oxidation and ageing could also be detected rapidly, and systematically followed. In certain cases this method of analysis was useful where ordinary methods failed, as for example, in the detection of the addition of refined olive oil, soya bean oil, and other adulterants to the natural olive oil."

Ultra-violet light has been utilized in recent years in "fluorescence analysis" for the following: (1) Tanning and paper manufacture. (2) Textile industries. (3) Colour and varnish industry. (4) Food stuffs (sugars, eggs, wines, fish, oils, fats, etc.). (5) Drugs and chemicals. (6) Medicine and bacteriology. (7) Rubber industry. (8) Mineralogy, petrology and palæontology. (9) Silicates (slags, ceramics, optical glasses etc.). (10) Fuels (coal, shale, shale oils etc.). (11) Criminology (testing banknotes, cheques, secret writings, customs examinations, authenticity of paintings, genuineness of precious stones etc.). (12) Testing of stamps (philately). (13) Testing photographic materials, gelatin etc.

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